CHAPTER 1

DPP 1.1

Subjective Type

1. (i) The SI unit of distance is metre (m).

1 mile = 1.60 kilometre = 1.60 × 1000 m

$$\text{Unit factor} = \frac{1.60 \times 100\ (\text{m})}{1\ \text{mile}} = \frac{1.6 \times 10^3\ (\text{m})}{1\ \text{mile}}$$

$$\therefore\ 93\ \text{million miles} = \frac{93 \times 10^6 (\text{miles}) \times 1.6 \times 10^3\ (\text{m})}{1\ \text{mile}}$$

$$= 93 \times 1.6 \times 10^9\ \text{m} = 148.8 \times 10^9\ \text{m} = 1.49 \times 10^{11}\ \text{m}$$

(ii) 5 feet 2 inches = 62 inches

$1\ \text{inch} = 2.54 \times 10^{-2}\ \text{m}$

$$\text{Unit factor} = \frac{2.54 \times 10^{-2}\ (\text{m})}{1\ \text{inch}}$$

$$62\ \text{inches} = \frac{62\ (\text{inches}) \times 2.54 \times 10^{-2}\ \text{m}}{1\ \text{inch}}$$

$$= 62 \times 2.54 \times 10^{-2}\ \text{m} = 157.48 \times 10^{-2}\ \text{m} = 1.57\ \text{m}$$

(iii) $1\ \text{mile} = 1.60\ \text{km} = 1.60 \times 10^3\ \text{m}$

$$\text{Unit factor} = \frac{1.60 \times 10^3\ \text{m}}{1\ \text{mile}}$$

$1\ \text{hr} = 60 \times 60\ \text{s} = 3.6 \times 10^3\ \text{s}$

$$\text{Unit factor} = \frac{3.6 \times 10^3\ \text{s}}{1\ \text{hr}}$$

$$\therefore\ \text{Speed} = \frac{100\ \text{miles}}{\text{hr}}$$

$$= \frac{100\ \text{miles}}{\text{hr}} \times \frac{1.60 \times 10^3 \text{m}}{1\ \text{mile}} \times \frac{1\ \text{hr}}{3.6 \times 10^3\ \text{s}} = 44\ \text{ms}^{-1}$$

(iv) $1\ \text{Å} = 10^{-10}\ \text{m}$.

$$\text{Unit factor} = \frac{10^{-10}\ \text{m}}{1\ (\text{Å})}$$

$$\therefore\ 0.74\ \text{Å} = \frac{0.74\ \text{Å} \times 10^{-10}\ (\text{m})}{1\ (\text{Å})}$$

$$= 0.74 \times 10^{-10}\ \text{m or } 7.4 \times 10^{-11}\ \text{m}$$

(v) 0°C = 273.15 K

46°C = 273.15 K + 46 K = 319.15 K

(vi) $1\ \text{pound} = 454 \times 10^{-3}\ \text{kg}$

$$\text{Unit factor} = \frac{454 \times 10^{-3}\ (\text{kg})}{1\ (\text{pound})}$$

$$\therefore\ 150\ \text{pound} = \frac{150\ (\text{pound}) \times 454 \times 10^{-3}\ (\text{kg})}{1\ (\text{pound})}$$

$$= 150 \times 454 \times 10^{-3}\ \text{kg} = 68.1\ \text{kg}.$$

2. (i) $$\frac{3.24 \times 0.08666}{5.006} = 0.05608 = 0.0561$$

In the calculation, the number of significant figures in the term 3.24 is 3, therefore, the result should have 3 significant figures. Therefore, the correct answer is 0.0561. The number after 0 is 8 and therefore it is rounded off to 1.

(ii) $$\frac{(1.36 \times 10^{-4})\ (0.5)}{2.6} = 0.2615 \times 10^{-4} = 0.3 \times 10^{-4}.$$

The answer should have one significant figure because 0.5 has one significant figure.

(iii) 0.582 + 324.65 (Second place of decimal)

325.232 = 325.23

Since 324.65 contains digits up to second place of decimal, therefore, the answer must reported up to second place.

(iv) $2.65 \times 10^3 + 3.27 \times 10^2$

or $2.64 \times 10^3 + 0.327 \times 10^3 = 2.97 \times 10^3$

Since 2.64 has two digits after decimal place, the answer should be rounded off to two decimal places.

(v) The first two numbers are to be multiplied initially as follows:

934 × 0.00345 = 3.25335 = 3.25.

According to the rules on multiplication of significant figures, the answer has to be reported up to three significant figures. It should be 3.25. Upon further addition, the final answer may be calculated as:

3.25 + 101 (zero place of decimal)

= 104.25 = 104.

3. Mass of piece of paper = 0.02 g

Mass of solid substance and piece of paper = 20.036 g

∴ Mass of solid substance = 20.036 – 0.02 = 20.016 or 20.02 (up to 2nd decimal)

Volume of solid = $2.16\ \text{cm}^3$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{20.02}{2.16} = 9.268$$

Since 2.16 has three significant figures, the answer should also contain three significant figures.

∴ Density up to proper number of significant figures = $9.27\ \text{g/cm}^3$.

Single Correct Answer Type

4. (d) $1\ \mu\text{g} = 10^{-6}\ \text{g}$

5. (c) Zeros to the left of the first non-zero digit in a number are significant.

6. (b) When numbers are written in scientific notation, the significant figures of only the first factor are counted.

7. (a) When numbers are written in scientific notation, the significant figures of only the first factor are counted.

8. (d) When addition is to be carried out in the numbers having different precisions, the final result should be reported up to the same number of decimal places as are present in the term having the least no. of decimal places.

9. (d) Nuclear radii is approximately of the order of 10^{-14} m.

10. (b) All non-zero digits and zero between non-zero digits are significant.

11. (b) 1 giga = 10^6.

Multiple Correct Answers Type

12. (a, d)

1 atm = 1.013 bar, 1 eV = 1.602×10^{-19} J

13. (a, b, c, d)

The zeros preceding to the first non-zero number are not significant.

All zeros placed at the end or to the right of a number are significant provided they are on the right side of the decimal point.

14. (a, c, d) Three

In exponential notations, the numerical portion represents the number of significant figure.

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In exponential notations, the numerical portion represents the number of significant figure.

All zeros placed at the end or to the right of a number are significant provided they are on the right side of the decimal point.

16. (a, c)

1 bar = 10^5 Pa

1 lb = 453.6 g

Matching Column Type

17. (a → s), (b → p), (c → q), (d → r), (e → u), (f → t)

Zeros to the left of the first non-zero digit in a number are significant.

In exponential notations, the numerical portion represents the number of significant figure.

As $\pi = \frac{22}{7} = 3.1428571$ ... hence, it has infinite number of significant figures.

1 femto = 10^{-15}

1 giga = 10^9

1 mega = 10^6

Integer Type

18. (3) A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL and 25.0 mL. The number of significant figures in the average titre value is 3. This is according to the rules of significant figures.

If two or more numbers having different precision are to be added or subtracted, the answer should be taken as the number of decimal places in the number having less decimal places.

19. (2) Up to 2 significant figures because the difference of 29.4 – 21.4 i.e., 8.0 contains 2 significant figures.

Comprehension Type

20. (a) Precision refers to the closeness of a set of values obtained for identical measurement of a quantity.

21. (b) All measured quantities are reported in such a way that only the last digit is uncertain usually by ±1.

22. (c) When addition is to be carried out in the numbers having different precisions, the final result should be reported up to the same number of decimal places as are present in the term having the least no. of decimal places.

23. (d) Zeros to the left of the first non-zero digit in a number are significant.

DPP 1.2

Subjective Type

1. The ratio between the different masses of dioxygen which combine with fixed mass of nitrogen (14 g) is

$$16 : 32 : 16 : 40$$

or

$$2 : 4 : 2 : 5$$

This is a simple whole number ratio and hence the data illustrate the law of multiple proportion.

2. In the first compound,

Percentage of phosphorus = 22.54

Percentage of chlorine = 77.46

Thus, 22.54 g of phosphorus combines with 77.46 g of chlorine.

In the second compound,

Percentage of phosphorus = 14.88

Percentage of chlorine = 85.12

Thus, 14.88 g of phosphorus combine with 85.12 g of chlorine.

Let us fix the mass of phosphorus as 1 g and find the different masses of chlorine which combine with 1 g of phosphorus in two compounds.

In the first compound,

Mass of chlorine which combines with 22.54 g of phosphorus = 77.46 g

The mass of chlorine which combines with 1 g of phosphorus

$$= \frac{77.46}{22.54} = 3.44 \text{ g}$$

In the second compound,

Mass of chlorine which combines with 14.88 g of phosphorus = 85.12 g

Mass of chlorine which combines with 1 g of phosphorus

$$= \frac{85.12}{14.88} = 5.72$$

The ratio of the masses of chlorine which combines with the fixed mass of phosphorus (1 g) in the two compounds is

3.44 : 5.72

1 : 1.66 or 3 : 5 (approximately)

This is a simple whole number ratio. Therefore, the data is in agreement with the law of multiple proportions.

3.

First oxide	**Second oxide**
Oxygen = 27.6%	Oxygen = 30%
Metal = 72.4%	Metal = 70%

Formula of first oxide = M_3O_4

Suppose the atomic weight of metal = x

Percentage of metal in the compound $M_3O_4 = \frac{3x}{3x+64} \times 100$

$$\therefore \quad \frac{3x}{3x+64} \times 100 = 72.4$$

or $\quad 300x = 217.2x + 4633.6$

or $\quad 82.8x = 4633.6$ or $x = 56$

Now in the second oxide, metal and oxygen are 70% and 30%. Therefore, their atomic ratio will be

	M	:	O
	$\frac{70}{56}$	:	$\frac{30}{16}$
	1.25	:	1.875
or	1	:	1.5
or	2	:	3

Therefore, formula of the compound = M_2O_3.

4. Molar mass = $N_A \times 3.257 \times 10^{-22}$ g.

Single Correct Answer Type

5. (d)

	First oxide	Second oxide
Sulphur	50%	40%
Oxygen	50%	60%

In first oxide 1 parts oxygen combines with sulphur = $\frac{50}{50} = 1$

Similarly for second oxide = $\frac{40}{60} = 0.67$

So the ratio is 1 : 0.67 or 3 : 2

6. (c) For fix mass of Fe, i.e., 56 parts, the masses of oxygen in these two oxides are 16 and 48 respectively, simple ratio is 1 : 3. So it is law of multiple proportion.

7. (c) $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

Value of $CO_2 = 3 \times 10$ mL

$= 30$ mL.

8. (b) Metal ⇒ Cation → A (138)

Non-metal ⇒ Anion ⇒ B (19)

Ionic compound = AB_2

∴ Formula mass (G.M.M. for ionic compound) = $138 + 2 \times 19$

$= 176$

9. (a)

Substance I	**C**		**O**
	27.27	:	72.73
mole	2.2725	:	4.5456
ratio	1	:	2
Substance II	52.94	:	47.06
mole	4.411	:	2.94
ratio	1.5	:	1.0
	3	:	1

10. (b) H_2S 5.89 g H combines with = 94.11 gS

Hence, 1 g H combines with = 16 g S

SO_2 50 g O combine with = 50 g S

Hence, 1 g O combines with = 1 g S

H_2O 11.11 g H combines with = 88.89 g O

1 gH combine with = 8 g O

Thus, law of reciprocal proportion is followed.

11. (b) $CO : CO_2 : C_2O_3\ (CO_{15})$

1 mol C = 12 g C in Co = 16 g O

= 12 g C in CO_2 = 32 g O

= 12 g C in C_2O_3 = 24 g O

Thus, ratio of O that combines with 12 g C = 2 : 4 : 3.

12. (b)

$\underset{50\%\ 50\%}{M\ O_2}$ 50 g ...... 1 metal

1 g ...... $\frac{1}{50}$

and 50 g ...... 2 oxygen

1 g ...... $\frac{2}{50}$ oxygen

$M_x\ O_y$

40 60

∴ 40 g ...... $\frac{4}{5}$ metal

For second oxide, Atoms of metal

$(M) = \frac{1 \times 40}{50} = 0.8$ similarly

Atoms of oxygen = $\frac{2 \times 60}{50} = \frac{12}{5} = 2.4$

Hence, ratio of M : O = 0.8 : 2.4 or 1 : 3

∴ Formula of the same metal oxide is MO_3.

13. (b) $N = 6.023 \times 10^{23} \times \frac{2}{100} = 1.20 \times 10^{22}$

Multiple Correct Answers Type

14. (a, d)

According to law of conservation of mass.

According to Avogadro's hypothesis.

15. (d)

(a) Not applicable if the elements exists in different isotopes which may be involved in the formation of compound.

(b) At 1 atm, 25°C molar volume = 22.7 L

(c) Mw = 2 × VD

(d) Due to existence of isotopes

16. (a, b, c, d) All are facts.

17. (b, c, d)

18. (a, b, d) According to law of multiple proportions.

19. (a, c)

(i) Atomic weight of Ca in new scale

$$= \frac{\text{mass of Ca}}{\frac{1}{6}\text{mass of C}} = \frac{40}{\frac{1}{6} \times 12} = 20\ \text{u}$$

(ii) Atomic weight of Ca in new scale

$$= \frac{\text{mass of Ca}}{\frac{1}{15} \times 12} = \frac{40}{12} \times 15 = 50$$

(iii) Atomic weight of Ca in new scale

$$= \frac{40}{\frac{1}{21} \times 12} = 70$$

(iv) Atomic weight of Ca in new scale

$$= \frac{40}{\frac{1}{30} \times 12} = 100$$

Matching Column Type

20. (a → r), (b → p, s), (c → q, t), (d → p, q, s, t)

$2NH_3 \longrightarrow N_2 + 3H_2$

$2HI \longrightarrow H_2 + I_2$

$O_3 \longrightarrow O_2 + \frac{1}{2}O_2$

$COCl_2 \longrightarrow CO + Cl_2$

$2HCl \longrightarrow H_2 + Cl_2$

Integer Type

21. (5) $$\underset{6.1\text{ g}}{NaHCO_3} + \underset{14.9\text{ g}}{CH_3COOH} \longrightarrow \underbrace{CH_3COONa + H_2O}_{\text{Residue }16.0\text{ g}} + \underset{x\text{g}}{CO_2}$$

- Sum of the mass of reactants

$= \text{Mass of } NaHCO_3 + \text{Mass of } CH_3COOH$

$= 6.1 + 14.9 = 21.0$ g

Sum of the mass of products = Mass of residue + Mass of CO_2

$= (16.0 + x)$g

According to law of conservation of mass,

Mass of reactants = Mass of products

$21.0 = 16.0 + x$

$x = 21.0 - 16.0 = 5.0$ g

∴ Mass of CO_2 released = 5.0 g.

22. (6) The average atomic mass $= \dfrac{y \times 35 + (100 - y)37}{100}$

But average atomic mass = 35.82

$\therefore \quad 35.82 = \dfrac{35y + 3700 - 37y}{100}$

$\Rightarrow \quad 3582 - 3700 = -2y$

$\Rightarrow \quad y = 59$

$\therefore \quad 100 - y = 41$

$\therefore \quad y = 6 \times 10^1$

$\therefore \quad x = 6$

Comprehension Type

23. (a) For $^{24}_{12}Mg$

24 g atom = 1 mol of Mg

1 g atom = 0.0416 mole

For $^{25}_{12}Mg$

25 g atom = 1 mol of Mg

1 g atom = 0.0400 mol

For $^{26}_{12}Mg$

26 g atom = 1 mol of Mg

1 g atom = 0.0384 mol.

24. (c) No. of neutrons

$^{24}_{12}Mg \quad 24 - 12 = 12$

$^{25}_{12}Mg \quad 25 - 12 = 13$

$^{26}_{12}Mg \quad 26 - 12 = 14$ (Max)

25. (b) Average atomic mass of Mg = (0.80)(24) + (0.05)(25) + (0.15)26

= 24.35 μ

DPP 1.3

Subjective Type

1. From question

$C \rightarrow 0.7 \times 15$

H – 15

0 – 1

or $C_{10.5}\,H_{15}\,O_1$

Empirical formula

i.e. $C_{21}\,H_{30}\,O_2$

2. ∵ 6.023×10^{23} molecules of $CO_2 \equiv 44$ g

$\therefore\ 10^{21}$ molecules of $CO_2 \equiv \dfrac{44 \times 10^{21}}{6.023 \times 10^{23}}\text{g} = 7.31 \times 10^{-2}$ g

= 73.1 mg

∴ CO_2 left ≡ 200 – 73.1 = 126.9 mg

Also, mole of CO_2 left $= \dfrac{\text{Mass}}{\text{molar mass}} = \dfrac{126.9 \times 10^{-3}}{44}$

$= 2.88 \times 10^{-3}$

3. Standard molar volume is the volume occupied by a mole of gas at NTP.

∵ 1.429 g of $O_2 \equiv 1$ litre at NTP

$\therefore$ 32 g of $O_2 \equiv \dfrac{32}{1.429}$ litre at NTP = 22.39 litre at NTP

∴ Molar volume = 22.39 litre mol^{-1}.

4. Let formula of alkane be C_nH_{2n+2}.

$$C_nC_{2n+2} + \left[n + \frac{n+1}{2}\right]O_2 \longrightarrow nCO_2 + (n+1)H_2O(l)$$

Given $\dfrac{\text{Volume of } O_2 \text{ used}}{\text{Volume of } CO_2 \text{ formed}} = \dfrac{7}{4}$

$\therefore \quad \dfrac{n + (n+1)/2}{n} = \dfrac{7}{4}$

$\therefore \quad n = 2$

∴ Alkane is C_2H_6.

5. Al = 10.50/27 = 0.39 = 0.39/0.39 = 1

K = 15.1/39 = 0.39 = 0.39/0.39 = 1

S = 24.96/32 = 0.78 = 0.78 / 0.39 = 2

$O = \dfrac{49.92}{16} = 3.12/0.39 = 8$

The empirical formula of the salt is $KAl\,S_2O_8$.

Empirical formula mass = 258

Let empirical formula mass = 100

Loss in weight due to removal of water = 45.6%

Therefore, the mass of the anhydrous salt = 54.4 a.m.u. When the anhydrous salt is 54.4, the hydrated salt is 100. If the anhydrous salt is 258, the hydrated one has mass

$= \dfrac{258 \times 100}{54.4} = 474.3$ a.m.u.

Therefore, the total actual loss of water = 474.3 – 258.0
= 216.3 a.m.u

Or, $\frac{216.3}{18}$ moles of water

Thus, the formula of the salt is K.Al. S_2O_8. 12 H_2O.

Single Correct Answer Type

6. (c) Minimum mol. wt. of insulin

$$= \frac{100}{3.4} \times 32 = 941.176 \text{ g/mole}$$

7. (c) Volume of $CO_2 = \frac{7.23 \times 10^{23}}{6.023 \times 10^{23}} \times 22.4 = 26.8$ L

Volume of Argon $= \frac{3.01 \times 10^{23}}{6.02 \times 10^{23}} \times 22.4 = 11.22$

Total volume = 26.8 + 11.2 = 38 L = 3.8×10^4 mL

8. (b) Moles of Zn $= \frac{9.61}{65.39} = 0.15$

Moles of Cr $= \frac{1.8 \times 10^{23}}{6.023 \times 10^{23}} = 0.3$

Moles of O = 0.6
So, whole molar ratio
= 0.15 : 0.3 : 0.6 = 1 : 2 : 4
Hence, formula = $ZnCr_2O_4$

9. (c) Mole of Al $= \frac{54}{27} = 2$

∴ Mass of Mg = 2 × 24 = 48 g.

10. (c)

	H_2	:	He	:	O_2	:	O_3
Ratio of total no. of molecules =	1	:	1	:	1	:	1
So ratio of total no. of atoms =	2	:	1	:	2	:	3

11. (b) Statement of Avogadro's hypothesis.

12. (b) $\frac{\text{Vapour density of A}}{\text{Vapour density of B}} = \frac{\text{Molar mass of A}}{\text{Molar mass of B}}$

Molar mass of A $= 2 \times \frac{M}{1}$

13. (c)

	A	B
Atomic mass	40	80
Given weight	x gram	$2x$ gram
No. of moles	$\frac{x}{40}$	$\frac{2x}{80}$
No. of atoms	$\frac{x}{40} \times N_A$	$\frac{x}{40} \times N_A$

But according to question $= \frac{x}{40} \times N_A = y$.

Multiple Correct Answers Type

14. (a, b, c)

Mole of $NH_3 = \frac{1.7}{17} = 0.1$ Mole of H atom = 0.3

Total atoms = $0.4 \times 6.02 \times 10^{23} = 2.408 \times 10^{23}$

Mass %H $= \frac{3 \times 1}{17} \times 100 = 17.65\%$.

15. (a, b, d)

$CH_3 - CH = CH - CH_3$
Total weight = 56

Carbon % $= \frac{48}{56} \times 100 = 86\%$

Same percentage in cyclohexane and 2-methyl but-2-ene.

16. (a, b)

$$n = \frac{w}{M} = \frac{V}{22.4}$$

$$\Rightarrow \frac{2}{3x} = \frac{448}{22.4}$$

$\Rightarrow x = 33.33$ atom
$= 33.33 \times 1.6 \times 10^{-24}$ g
$= 5.53 \times 10^{-23}$ g

17. (a, b, c, d)

(a) $n_{NH_3} = \frac{4.25}{17} = 0.25$

(b) $NH_3 \equiv 3$ H
1 mole ≡ 3 moles of H atom
0.25 mole ≡ 3 × 0.25 mole of H atom = 0.75 mole of H atom

(c) Total moles of atoms = $n_N + n_H$ atoms
= 0.25 + 0.75 = 1 mole of atom

(d) No. of molecules = $0.25 \times N_A$
$= 0.25 \times 6.023 \times 10^{23} = 1.5 \times 10^{23}$

18. (a, b, c)

(a) No. of O_2 molecules $= \frac{1}{32} \times N_A$

No. of SO_2 molecules $= \frac{2}{64} \times N_A$

(b) No. of CO_2 molecules $= \frac{1}{44} \times N_A$

No. of N_2O molecules $= \frac{1}{44} \times N_A$

(c) No. of O_2 molecules $= \frac{N_A}{224} \times 112 = \frac{N_A}{2}$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{0.5 \times 224}{273} = \frac{1 \times V_2}{273}$$

$\Rightarrow V_2$ at STP = 112 mL
⇒ 224 mL at STP has N_A

112 mL at STP has $\frac{N_A}{224} \times 112 = \frac{N_A}{2}$

(d) No. of O_2 molecules $= \frac{1}{32} \times N_A$

No. of O_3 molecules $= \frac{1}{3 \times 16} \times N_A$

19. (a, b, c, d)

(a) NH_3 for 1 mole = 4 moles of atoms
For 3 mole = 4 × 3 = 12 moles of atoms
= 12 × N_A moles of atoms

(b) Vol. at STP for 1 mole = 22.4 L
For 3 moles = 67.2 L

Matching Column Type

20. **(a → r), (b → q), (c → p)**

(a) 176 g of vitamin C has $6 \times N_A$ of 'O' atoms

$$17.6 \times 10^{-3} \text{ g of vitamin has} = \frac{6 \times N_A}{176} \times 17.6 \times 10^{-3} = 3.6 \times 10^{20}$$

(b) $n = \frac{1}{176} = 5.68 \times 10^{-3}$

(c) $\frac{W}{M} = \frac{17.6 \times 10^{-3}}{176} = 10^{-4}$

Integer Type

21. (8) Molar mass of $Na_2SO_4 \cdot nH_2O = (142 + 18n)$

$$\% \text{ Loss in mass} = \frac{18n}{(142 + 18n)} \times 100$$

$$50.3 = \frac{18n \times 100}{142 + 18n}$$

$n = 8.$

22. (3) $\frac{5.1}{17} = 0.3$ mole

No. of electrons $= 10 \times 0.3\ N_A = 3\ N_A$.

23. (8) 100 g of protein has 0.07 g of Fe.

So, 56 g of Fe should have minimum weight of $\frac{100}{0.07} \times 56 = 80000 = 8 \times 10^4$ g

Comprehension Type

Q. 24 to Q. 25

Element	%	$\frac{\%\text{ mass}}{\text{At. mass}}$		
Al	10.5	$\frac{10.5}{27}$	0.388	1
K	15.1	$\frac{15.1}{39}$	0.387	1
S	24.8	$\frac{24.8}{32}$	0.775	2
O	49.6	$\frac{49.6}{16}$	3.1	8

∴ Empirical formula $= KAlS_2O_8$

Assume molecular formula of hydrated salt $= KAlS_2O_8 . xH_2O$

then $\frac{18x}{39 + 27 + 128 + 18x} \times 100$

$= 45.6 \Rightarrow x = 12.$

26. (a) $76.6 = \frac{46a + (100 - a)92}{100}$

$a = 33.48$

27. (a) $He = \frac{4}{4} \times N_A$

$O_2 = \frac{4}{32} \times N_A \times 2$

$O_3 = \frac{4}{48} \times N_A \times 3$

$H_2O_2 = \frac{4}{34} \times N_A \times 4$

DPP 1.4

Subjective Type

1. Empirical formula $= XY_2Z_3$

According to the Ques.

$$\begin{array}{lcccccc} & X & + & 2Y & + & 3Z \rightarrow XY_2Z_3 \\ & 5.00 \text{ g} & & 1.15 \times 10^{23} \text{ atom} & & 0.03 \text{ moles} \\ \text{or} & \frac{5}{60} \text{ moles} & & \frac{1.15 \times 10^{23}}{6.023 \times 10^{23}} \text{ mole} & & 0.03 \text{ moles} \\ \text{or} & 0.083 \text{ mole} & & 0.191 \text{ mole} & & 0.03 \text{ moles} \end{array}$$

It is clear that here Z is limiting reagent.

$$\begin{array}{lccccccc} \text{Hence} & X & + & 2Y & + & 3Z & \rightarrow & XY_2Z_3 \\ & & & & & 0.03 & & 0.01 \text{ mole} \end{array}$$

According to the condition,

0.01 mole = 4.40 g

1 mole = 440 g

Given that atomic wt. of X and Z are 60 and 80 amu respectively.

Hence

$60 + 2y + 3 \times 80 = 440$

or $2y + 60 + 240 = 440$

or $2y = 440 - 300$

or $y = \frac{140}{2} = 70$

Atomic wt. of $y = 70$ amu.

2. Balancing the given equation

$$\begin{array}{lccccccc} & 2VO & + & 3Fe_2O_3 & \rightarrow & 6FeO & + & V_2O_5 \\ \text{Mole before reaction} & \frac{2}{67} & & \frac{5.75}{160} & & & & \\ & = 0.0298 & & = 0.0359 & & 0 & & 0 \\ \text{Mole after reaction} & \left(0.0298 - \frac{0.0359 \times 2}{3}\right) & & 0 & & 0.0359 \times 2 & & 0.0359 \times \frac{1}{3} \end{array}$$

∴ Mole of FeO formed $= 0.0359 \times 2$

∴ Mass of FeO formed $= 0.0359 \times 2 \times 72 = 5.17$ g

The limiting reagent is one which is used completely, i.e., Fe_2O_3 here.

3. 76 kg of CS_2

SO_2 that converted $= 440 \times \frac{80}{100}$ kg $= 352$ kg

$$\begin{array}{lccccccc} & 5C & + & 2SO_2 & \longrightarrow & CS_2 & + & 4CO \\ \text{Initial mole} & 5 \times 10^3 & & \frac{352}{64} \times 10^3 & & 0 & & 0 \\ & & & = 5.5 \times 10^3 & & & & \end{array}$$

$$\begin{array}{lllll} \text{Final mole} & 0 & 5.5\times10^3 & 1\times10^3 & 4\times10^3 \\ & & -\frac{2}{5}\times5\times10^3 & & \end{array}$$

Mole of CS_2 = 1000

Mass = 1000 × 76 g = 76 kg

4. (i) Calculation of H_2 required to reduce CuO to Cu.

$$\begin{array}{cccc} CuO & + & H_2 & \longrightarrow Cu + H_2O \\ 1\text{ mol} & & 1\text{ mol} & \\ 63.5+16=79.5\text{ g} & & 2\text{ g} & \end{array}$$

One mole of CuO require 1 mole of H_2 for reduction to copper or 79.5 g of CuO require H_2 for reduction to copper = 2 g

8.5 g of CuO require H_2 for reduction to copper $= \frac{2}{79.5}\times 8.5$
$= 0.214$ g

(ii) Calculation of weight of zinc required to produce H_2.

$$\begin{array}{ll} Zn + H_2SO_4 \longrightarrow ZnSO_4 + & H_2 \\ 1\text{ mol} & 1\text{ mol} \\ 65\text{ g} & 2\text{ g} \\ \text{g} & 0.214\text{ g} \end{array}$$

2 g of H_2 is produced from zinc = 65 g

0.214 g of H_2 would be produced from zinc $= \frac{65}{2}\times 0.214$
$= 6.955$ g

5. Gas + Sn $\longrightarrow$ SnS + H_2

Mole of gas $= \frac{200}{22400} = 9\times10^{-3}$

$H_2 + CuO \longrightarrow Cu + H_2O$

Mole of $H_2O = \frac{0.162}{18} = 9\times10^3$ = mole of H_2

9×10^{-3} mole gas contain = 9×10^{-3} mole H_2

∴ 1 mole gas has = 1 mole of H_2
= 2 mole 'H' atom

Molar mass $H_2S_x = 2\times17 = 2\times1 + x(32)$

$x = \frac{34-2}{32} = 1$

So, gas is H_2S.

Single Correct Answer Type

6. (a)

$$\begin{array}{lcccc} & C & + & CO_2 & \longrightarrow 2CO \\ \text{Given moles} & \left(\frac{6}{12}\right)=0.5 & & \left(\frac{44}{44}\right)=1 & \end{array}$$

So C is limiting reagent.

∴ CO formed = 1 mole

Now moles of Ni needed to react with 1 moles of CO are

$\frac{1}{4}\times 58.7 = 14.675$ g

7. (c)

$$\begin{array}{lcccc} & 2X & + & 3Y & \longrightarrow X_2Y_3 \\ \text{Weight} & W\text{ gram} & & W\text{ gram} & 0 \\ \text{Mole} & \frac{w}{36} & & \frac{w}{24} & \\ \text{L.R.}\rightarrow & \frac{w}{36}\times\frac{1}{2} & & \frac{2}{24\times3} & \\ & \frac{1}{72} & & \frac{1}{72} & \end{array}$$

Number one is L.R.

$$\begin{array}{cccc} 2X & + & 3Y & \longrightarrow X_2Y_3 \\ \frac{w}{36} & & \frac{w}{24} & \frac{w}{2[36]} \end{array}$$

Weight of $X_2Y_3 = \frac{w}{2\times36}[72\times2] = 2w$

So weight of X_2Y_3 = 2 [weight of X taken]

8. (a)

$$\begin{array}{lccccc} & TiCl_4 & + & 2Mg & \longrightarrow Ti & + 2MgCl_2 \\ \text{Initial mole} & \frac{358}{190}=1.88 & & \frac{96}{24}=4 & & \\ \text{Final mole} & 0 & & 4-2\times1.88 & 1.88 & 2\times1.88 \end{array}$$

Wt. of Ti obtained $= \frac{358}{190}\times48$

% yield $= \frac{32\times100}{\frac{358\times48}{190}} = 35.38\%$

9. (a) $M + X_2 \longrightarrow MX_2$

$MX_2 + X_2 \longrightarrow M_3X_8$

$M_3X_8 + Na_2CO_3 \longrightarrow NX + CO_2 + M_3O_4$

Mole of NX $= \frac{206}{103} = 2$

POAC for X atom

No. of x atom in M_3X_8 = No. of X atom in NX

8[No. of mole of M_3X_8] = 1[No. of mole of NX]

No. of mole of $M_3X_8 = \left[\frac{2}{8}\right] = \frac{1}{4}$ mole

Now, POAC for M atom

3[No. of mole of M_3X_8] = 1 × [No. of mole of M]

∴ $3\times\frac{1}{4}$ = No. of mole of M

Weight of M atom $= \frac{3}{4}\times56 = 42$ gram

10. (b) Balanced equation:

$NaI + AgNO_3 \longrightarrow AgI + NaNO_3$ (1

$2AgI + Fe \longrightarrow FeI_2 + 2Ag$ (2

$2FeI_2 + 3Cl_2 \longrightarrow 2FeCl_3 + 2I_2$ (3

From (3)

$\frac{\text{mole of } I_2}{2} = \frac{\text{mole of } FeI_2}{2}$

$\frac{\text{mole of } FeI_2}{1} = \frac{\text{mole of AgI}}{2}$

$\frac{\text{mole of AgI}}{1} = \frac{\text{mole of } AgNO_3}{1}$

∴ mole of I_2 = (mole of FeI_2)

$\left(\frac{\text{mole of AgI}}{2}\right) = \left(\frac{\text{mole of } AgNO_3}{2}\right)$

$\frac{254\times10^3}{254} = \frac{\text{mole of } AgNO_3}{2}$

2×10^3 = mole of $AgNO_3 = \frac{\text{mass of } AgNO_3}{\text{molar mass of } AgNO_3}$

Mass of $AgNO_3 = 170\times(2\times10^3)$ g $= 340\times10^3$ g = 340 kg.

11. (a) In this problem, CO_2 can be calculated by using either of the reactants $CaCO_3$ or HCl. So, first of all we are to calculate the limiting reactant.

$$\underset{\substack{1\text{ mol}\\40+12+3\times16\\=100\text{ g}}}{CaCO_3(s)} + \underset{\substack{2\text{ mol}\\2\times(1+35.5)\\=73\text{ g}}}{2HCl(aq)} \longrightarrow CaCl_2(aq)+H_2O(l)+CO_2(g)$$

According to above equation,

100 g of $CaCO_3$ requires 73 g of HCl.

$$20\text{ g of }CaCO_3\text{ require} = \frac{73}{100}\times 20 = 14.6\text{ g}$$

But amount of HCl actually present = 20.0 g

Therefore, $CaCO_3$ is limiting reactant and HCl is excess reactant.

Now let us calculate the amount of CO_2 produced when entire quantity of limiting reactant reacts.

$$\underset{\substack{1\text{ mol}\\100\text{ g}\\20\text{ g}}}{CaCO_3(s)} + 2HCl(g) \longrightarrow CaCl_2(aq) + H_2O(l) + \underset{\substack{1\text{ mol}\\44\text{ g}\\?}}{CO_2(g)}$$

100 g of $CaCO_3$ produces CO_2 = 44 g

$$20\text{ g of }CaCO_3\text{ will produce }CO_2 = \frac{44}{100}\times 20 = 8.80\text{ g}$$

Multiple Correct Answers Type

12. (a, d)

$$\overset{1}{Mg} + \overset{2}{2HCl} \longrightarrow Mg\,Cl_2 + H_2\uparrow$$

2.4/24 (0.1 mole) ↓ 100 mL, 1 m mol/L

100×10^{-3} = 1 mole → 5 mole consumed

H_2: 0.1 mole ↓ 0.05 mole

HCl is limiting reagent, its 0.1 mole will be consumed. Hence 0.5 mole Mg^{2+} ions will be used, i.e., 0.05 mole ⇒ 1.12 L Hydrogen will be produced.

13. (b, d)

	3A	+	2B	⟶	A_3B_2
Initial mole	3		3		0
Final mole	0		3 − 2		1

	A_3B_2	+	2C	⟶	$A_3B_2C_2$
Initial mole	1		1		0
Final mole	$1-\frac{1}{2}$		0		$\frac{1}{2}$

14. (b, c, d)

	C	+	O_2	⟶	CO_2
Mass	27		88		
Moles	$\frac{27}{12}$		$\frac{88}{32}$		

C is limiting reagent.

$$\text{Moles of }CO_2\text{ produced} = \text{moles of C} = \frac{27}{12} = 2.25$$

∴ Volume of CO_2 at STP = 2.25 × 22.4 = 50.4 L

Ratio of C and O in CO_2 = 12 : 32 = 3 : 8

Moles of unreacted O_2 = 2.75 − 2.25 = 0.5

∴ Volume of unreacted O_2 at STP = 0.5 × 22.4 = 11.2 L

15. (b, c)

$$n_{H_2} = \frac{64}{2} = 32\text{ mol}$$

$$n_{O_2} = \frac{64}{32} = 2\text{ mol}$$

1 mol of O_2 requires = 2 mol of H_2

2 mol of O_2 requires = 4 mol g of H_2

Since H_2 is present in excess, therefore, O_2 is the limiting reagent.

(a) Wrong.

(b) So, O_2 is the limiting reagent.

(c) 2 mol of O_2 = 4 moles of H_2O = 4 × 18 = 72 g H_2O

Moles of H_2 left = 32 − 4 = 28 mol = 28 × 2 = 56 g H_2

Mixture contains = (72 g H_2O + 56 g H_2)

(d) Wrong.

16. (a, b, c, d)

(Mw of Na_2CO_3 = 106, Mw of HCl = 36.5, Mw of NaCl = 58.5)

$$\text{Moles of }Na_2CO_3 = \frac{106}{106} = 1.0\text{ mol}$$

$$\text{Moles of HCl} = \frac{109.5}{36.5} = 3.0\text{ mol}$$

(a) Since for 1 mol of Na_2CO_3, 2 mol of HCl is required. S

HCl is in excess (3 − 2) = 1.0 mol

Therefore, Na_2CO_3 is the limiting quantity.

(b) Weight of NaCl formed

$$= (1.0\text{ mol }Na_2CO_3)\left(\frac{2\text{ mol NaCl}}{\text{mol }Na_2CO_3}\right)\left(\frac{58.5\text{ g NaCl}}{\text{mol NaCl}}\right)$$

= 1 × 2 × 58.5 = 117.0 g NaCl

(c) 1 mol of Na_2CO_3 = 1 mol of CO_2 = 22.7 L at 1 bar, 273

(d) 1 mol of Na_2CO_3 = 1 mol of CO_2 = 24.7 L at 1 bar, 298

Matching Column Type

17. (a → r), (b → s), (c → p), (d → q)

(a → r); Here oxygen is limiting reagent. 32 g of oxygen giv 36 g of H_2O

$$1\text{ g of oxygen gives }\frac{36}{32} = 1.125\text{ g}$$

(b → s); Here N_2 is limiting reagent. 28 g of N_2 gives 34 g NH_3

$$1\text{ g of }N_2\text{ gives }\frac{34}{28} = \frac{17}{14} = 1.214\text{ g of }NH_3$$

(c → p); Here $CaCO_3$ is limiting reagent. 100 g of $CaCO_3$ gi 56 g of CaO

$$1\text{ g of }CaCO_3\text{ gives }\frac{56}{100} = 0.56\text{ g of CaO}$$

(d → q); Here carbon is limiting reagent. 12 g of C gives of methane

$$1\text{ g of C gives }\frac{16}{12} = 1.33\text{ g}$$

Integer Type

18. (4)

$$\begin{array}{cccc} 2H_2 & + & O_2 & \longrightarrow 2H_2O \\ 10\text{ g} = 5\text{ mol} & & 64\text{ g} = 2\text{ mol} & \end{array}$$

Limiting reagent is O_2.

1 mole of O_2 gives 2 moles of H_2O

$\therefore$ 2 moles of O_2 will give 4 moles of H_2O.

19. (2)

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$n_{H_2} = \frac{5}{2} = 2.5 \qquad n_{N_2} = \frac{14}{28} = 0.5$$

1 mole of N_2 reacts with 3 moles of H_2.

0.5 mole of N_2 reacts with 1.5 moles of H_2.

$\Rightarrow n_{H_2}$ unreacted $= 2.5 - 1.5 = 1$ mole

$\Rightarrow 2$ g.

Comprehension Type

20. (b) K_2PtCl_4 is L.R. Hence it will be completely consumed.

21. (a) Moles of ammonia will consumed twice that of K_2PtCl_4.

22. (c) $0.58 - 0.04 = 0.54$

No. of moles of NH_3 which is unreacted.

DPP 1.5

Subjective Type

1. (a) 2.35 ppm means

10^6 g of water contains = 2.35 g of Ca

or 10^6 mL of water contains = 2.35 g of Ca

($\therefore d_{\text{water}} = 1$ g/cc)

1 mL water contains $= \frac{2.35}{10^6}$

50 mL water contains $= 2.35 \times 10^{-6} \times 50$

or 50 mL water contains $= 117.5 \times 10^{-6}$ g

No. of moles of Ca in 50 mL of water

$$= \frac{117.5 \times 10^{-6}}{40}$$

$$= 2.9375 \times 10^{-6} \text{ moles}$$

Hence there should be 2.9375×10^{-6} moles of $Ca(NO_3)_2$ in 50 mL water.

Wt. of $Ca(NO_3)_2$ in 50 mL water

= No. of moles × Mol. wt.

$= 2.9375 \times 10^{-6} \times (164)$

$= 481 \times 10^{-6}$ g

$= 481 \times 10^{-6} \times 10^3$ mg

$= 481 \times 10^{-3}$ mg $= 0.48$ mg

(b) It is clear that

10^6 g of water contains 1.52 g of Na.

Given that $d_w = 1$ g/cc

Hence 10^6 mL of water contains 1.52 g of Na.

1 mL of water contains $\frac{1.52}{10^6}$ g.

1000 mL of water contains $1.52 \times 10^{-6} \times 1000$ g of Ca

or 1 L of water contains 1.52×10^{-3} g of Ca

No. of moles of Na $= \frac{\text{wt. in gram}}{\text{At. wt}} = \frac{1.52 \times 10^{-3}}{23}$

$= 0.066087 \times 10^{-3}$ moles

Hence, there are 6.6087×10^{-5} mole of Na or NaCl in 1 litre water.

The molarity of solution $= 6.6087 \times 10^{-5}$ M NaCl.

2.

$$\begin{array}{llll} NaCl & \rightarrow Na^+ & + & Cl^- \\ 0.2\text{ M} & \quad 0.2\text{ M} & & 0.2\text{ M} \\ Na_2SO_4 & \rightarrow 2Na^+ & + & SO_4^{-2} \\ 0.1\text{ M} & \quad 2 \times 0.1\text{ M} & & 0.1\text{ M} \\ & \quad = 0.2\text{ M} & & \end{array}$$

Ionic strength of Na^+ in solution

$= 0.2 \times 23 + 0.2 \times 23$

$= 9.2$ g/L

Ionic strength of Cl^-

$= 0.2 \times 35.5$

$= 7.10$ g/L

Ionic strength of SO_4^{-2}

$= 0.1 \times 96$

$= 9.6$ g/L

3. Volume of $HNO_3 = 50$ mL, density = 1.5

$d = \frac{M}{V}$, mass of solution $= 50 \times 1.5$

Weight of $HNO_3 = \frac{75 \times 63}{100} = \frac{3}{4} \times 63$

Mole of $HNO_3 = \frac{3}{4} \times \frac{63}{63} = \frac{3}{4}$ mole

$$M = \frac{\text{Mole of } HNO_3}{\text{Volume of solution}} = 1 = \frac{3}{4 \times V_{\text{lit}}} = 1$$

$$V = \frac{3}{4}\text{ lit} = 750 \text{ mL}$$

Volume of water added $= 750 - 50 = 700$ mL

4. $K_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2KCl$

Mole of $BaSO_4 = \frac{2.33}{233} = \frac{1}{100}$

Mole of K_2SO_4 used $= \frac{1}{100}$

Molarity of K_2SO_4 solution $= \frac{5/174}{1/4} = \frac{20}{174}$

Least volume of K_2SO_4 solution is V.

$$\frac{1}{100} = M \times V$$

$$V = \frac{1}{100} \times \frac{174}{200} = 0.087 \text{ litre} = 87 \text{ mL}$$

5. Let the volume of solution is 1 litre.

$\therefore$ moles of $CaCl_2 = 5$ moles of $Cl^- = 10$

Mass of $CaCl_2$ in solution $= 5 \times 111 = 555$ g

Let mass of $MgCl_2$ is x g.

So, total mass of 1 litre solution $= 555 + x + w_{H_2O}$

$= 1000 \times 1.05 = 1050$

$\therefore \; w_{H_2O} = (495 - x)$ g

Given, molality of $MgCl_2 = 5$ m

$$\left(\frac{x/95}{495 - x}\right) \times 1000 = 5$$

On solving, we get

$x = 159.4$

$\therefore$ moles of $MgCl_2 = \dfrac{159.4}{95} = 1.68$

$\therefore$ mole of $Cl^- = 3.36$

Total moles of $Cl^- = 10 + 3.36 = 13.36$ in 1 litre solution.

Single Correct Answer Type

6. (b) Mole fraction of $I_2 = X_A$

$X_A = \dfrac{n_1}{n_1 + n_2}$ $\qquad$ $X_B = \dfrac{n_2}{n_1 + n_2}$

$X_A + X_B = 1$

$X_A = 0.2$

$X_B = 0.8$

$\dfrac{X_A}{C_B} = \dfrac{n_1}{n_2}$

$n_1 : n_2 = 1 : 4$

Mass of solvent

$\because \; n_2 = \dfrac{w}{M}$

$w = n_2 \times M = 4 \times 78(g)$

Molality $= \dfrac{n_1}{\text{mass of solvent (in kg)}}$

$= \dfrac{1}{4 \times 78} \times 1000 = 3.21$ m

7. (c) No. of equivalents of acid (HCl) is greater than no. of equ. base, so that solution is acidic.

No. of equivalents of Base $= N_1V_1$

$V_1 = 125$ mL

$N_1 = \dfrac{w}{E} \times \dfrac{1000}{100}$

$= \dfrac{10}{40} \times \dfrac{1000}{100} = 2.5$

$N_1V_1 = 2.5 \times 125$

No. of equivalents of acid $= N_2V_2$

$V_2 = 125$

$N_2 = \dfrac{10}{35.5} \times \dfrac{1000}{100}$

$= \dfrac{100}{35.5} = 2.82$

$N_2V_2 = 2.82 \times 125$

$\boxed{N_2V_2 > N_1V_1}$

8. (b) Weight of KOH = 2.8 gram

Volume of solution = 100 mL

$$M = \frac{2.8 \times 1000}{56 \times 100} = \frac{28}{56} = 0.5 \text{ M}$$

9. (a)

$$\begin{array}{ccccc} M_1V_1 & + & M_2V_2 & = & M_R[V_1 + V_2] \\ 1 \times 500 & & 1 \times 500 & = & M_R[500 + 500] \\ & & & & M_R = 1 \end{array}$$

10. (d)

$m = 0.2$ mole/kg

Weight of solvent = 1000 gram

Weight of solute $= 0.2 \times 98 = 19.6$ gram

Total weight of solution $= 1000 + 19.6 = 1019.6$ mL.

11. (d) V_1 mL 0.2 M NaCl, V_2 mL 0.1 M $CaCl_2$

(+ve ion) $= 0.2\,V_1 = 0.1\,V_2$ mole

(–ve ion) $= 0.2\,V_1 + 0.1 \times 2\,V_2$

$= 0.2\,V_1 + 0.2\,V_2$ mole

By equation,

$(+ve) = (-ve) - (-ve) \times \dfrac{40}{100}$

$= (-ve) \times \dfrac{60}{100}$

$\Rightarrow \; 0.2\,V_1 + 0.1\,V_2 = 0.2\,(V_1 + V_2) \times \dfrac{6}{10}$

$\Rightarrow \; 2\,V_1 + V_2 = 1.2\,V_1 + 1.2\,V_2$

$\Rightarrow \; 0.8\,V_1 = 0.2\,V_2\; 4\,V_1 = V_2$

$V_1 = 200$ mL, $V_2 = 800$ mL.

Multiple Correct Answers Type

12. (a, c)

$$[SO_2Cl_2] = \frac{2.70 \times 1000}{135 \times 100}$$

$= 0.2$ M

$$\begin{array}{cccc} SO_2Cl_2 + 2H_2O & \rightarrow & H_2SO_4 & + \; 2HCl \\ 100 \times 0.2 & & & \\ = 20 & & 0 & 0 \\ 0 & & 20 & 40 \end{array}$$

$\therefore \; M_{H_2SO_4} = \dfrac{20}{100}; \; M_{HCl} = \dfrac{40}{100}$

$\therefore \; N_{H_2SO_4} = 0.4$ and $N_{HCl} = 0.4$

13. (a, c)

3.42 ppm $Al_2(SO_4)_3$

$= \dfrac{96 \times 3 \times 3.42}{342}$ ppm $[SO_4^{2-}] = 2.88$ ppm SO_4^{2-}

$= \dfrac{27 \times 2 \times 3.42}{342}$ ppm $Al^{3+} = 0.54$ ppm Al^{3+}

1.42 ppm $Na_2SO_4 = \dfrac{96 \times 1.42}{142}$ ppm $SO_4 = 0.96$ppm SO_4^{2-}

$= \dfrac{46 \times 1.42}{142}$ ppm $Na^+ = 0.46$ ppm Na^+

$\therefore \; [Al^{3+}] = \dfrac{0.54 \times 10^3}{27 \times 10^6} = 2.0 \times 10^{-5}$ M

$$[SO_4^{2-}] = \frac{(2.88+0.96)\times 10^3}{96\times 10^6} = 4\times 10^{-5}\ M$$

$$[Na^+] = \frac{0.46\times 10^3}{23\times 10^6} = 2\times 10^{-5}\ M$$

14. (a, b, c)

Mole fraction of solute and solvent change with dilution, however mole of solute remains constant and mole fraction of solute decreases with dilution, mole of solute and molality does not change with temperature.

15. (a, d)

The mass of 1000 mL solution will be (1000 mL) (1.09 g mL^{-1}) = 1090 g. The mass of sulphuric acid in the solutions (13/100) (1090 g) = 141.7 g. Amount of sulphuric acid is 141.7 g/98 g mol^{-1} = 1.446 mol. Hence,

$$\text{Molarity of } H_2SO_4 = \frac{1.446\ \text{mol}}{1\text{L}} = 1.446\ \text{mol L}^{-1}$$

$$\text{Molarity of } H_2SO_4 = \frac{1.446\ \text{mol}}{(1090-141.7)\times 10^3\ \text{kg}} = 1.525\ \text{mol kg}^{-1}.$$

16. (a, b, d)

Mixture contain two moles of H^+, so it can be neutralized by 2 mol of OH^- ion (i.e. a, b, d).

Matching Column Type

17. (a → q), (b → p), (c → r), (d → s)

(a → q): millimoles of Zn $= \frac{196.2\ \text{mg}}{65.4\ \text{mg}} = 3$ m mol

3 m mol of Zn ≡ 2 m mol of $[Fe(CN)_6]^{4-} \equiv \frac{2\ \text{m mol}}{40\ \text{mL}}$

$= 0.05$ M

(b → p): Moles of $BaSO_4 = \frac{2.33}{233} = 0.01$ mol

$= 0.01$ mol Na_2SO_4

$$M_{Na_2SO_4} = \frac{\text{m mol}}{\text{mL}} = \frac{0.01\times 10^3}{40} = 0.25\ M$$

(c → r): m mol of $Th^{4+} = \frac{116\ \text{mg}}{232\ \text{mg}} = 0.5$ m mol

$= 0.5\times 2\times$ m mol of $H_2C_2O_4$

$$M_{H_2C_2O_4} = \frac{\text{m mol}}{\text{mL}} = \frac{0.5\times 2}{50} = 0.02\ M$$

(d → s): m mol of $AgNO_3 = 10\times 0.5 = 5$ m mol

$= 2\times 5$ m mol of NaCN

$$M_{NaCN} = \frac{\text{m mol}}{\text{mL}} = \frac{2\times 5}{100} = 0.1\ M$$

Integer Type

18. (2) $M_1V_1 = N_2V_2$ (Atomic weight of Co = 58.93 g)

$$= \frac{100\ \text{mg}}{58.93\ \text{mg}}\times V_1 = \frac{20\ \text{mg}}{58.93\ \text{mg}} = \times 10\ \text{mL}$$

$$V_1 = \frac{20\times 10}{100} = 2\ \text{mL}$$

19. (9) $M = \frac{\%\text{ by weight}\times 10\times d}{M_{w_2}} = \frac{30\times 10\times 1.095}{36.5} = 9\ M$

20. (2) $M_1V_1 = M_2V_2$

$2\times x = 1\times 4$

$x = 2$

Comprehension Type

21. (b) Strength of HNO_3 = 70%

Volume of solution = 100 mL

and Volume of HNO_3 = 70 mL

∴ Mass of HNO_3 in solution = 70 × 1.42 g

∴ Eq. of HNO_3 in solution $= \frac{70\times 1.42}{63}$

$$\therefore\ N_{HNO_3} = \frac{70\times 1.42}{63\times 100/1000} \qquad \left(\because N = \frac{\text{Eq.}}{V\text{ in litre}}\right)$$

$= 15.78$

22. (c)

∵ 70 × 1.42 g of pure acid is present in 100 mL

∴ 63 g of acid present in $= \frac{100\times 63}{70\times 1.42} = 63.38$ mL

23. (a) Meq. of conc. HNO_3 = Meq. of dil. HNO_3

(∵ Meq. does not change on dilution)

∴ $2\times 15.78 = V\times 1$

∴ $V = 31.56$ mL

∴ Volume of water added = 31.56 – 2 = 29.56 mL.

DPP 1.6

Subjective Type

1. The reduction half reaction is

$$\underset{\text{oxalate ion}}{C_2O_4^{2-}} \longrightarrow 2CO_2 + 2e^-$$

$$\therefore\quad \text{Eq. wt. of } C_2O_4^{2-} = \frac{2\times 12 + 4\times 16}{2} = 44$$

Let N_1 be the normality of the oxalate solution. Applying normality equation, we have

$$15\times \frac{1}{20}(KMnO_4) = N_1\times 10\ (C_2O_4^{2-})$$

$$\therefore\ N_1 = \frac{15}{10\times 20} = \frac{3}{20}\ N$$

Strength of oxalate solution = Normality × Eq. wt.

$= \frac{3}{40}\times 44 = 3.3$ g/litre

∴ Amount of pure $C_2O_4^{2-}$ present in 100 mL $= \frac{3.3}{1000}\times 100$

$= 0.33$ g

But amount of $C_2O_4^{2-}$ present in impure sample = 0.5 g (Given)

∴ Percentage of pure oxalate $= \frac{0.33}{0.50}\times 100 = 66$

2. The balanced redox reaction involving oxidation of Fe^{2+} ions by $Cr_2O_7^{2-}$ and MnO_4^- respectively are:

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 5Fe^{3+} + 7H_2O$ and

$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+}\ 4H_2O$

Suppose V_2 cm^3 of is titrated against 24.50 cm^3 of 0.1 M $Cr_2O_7^{2-}$ and V_1 cm^3 of 0.1 M MnO_4^- solutions, then

$$\frac{24.5 \times 0.1}{1}(Cr_2O_7^{2-}) = \frac{M_2V_2}{6}(Fe^{2+}) \qquad (1)$$

$$\text{and} \quad \frac{V_1 \times 0.1}{1}(MnO_4^-) = \frac{M_2V_2}{5}(Fe^{2+}) \qquad (2)$$

Equating (1) and (2), $V_1 = 24.5 \times \frac{6}{5} = 29.4\ \text{cm}^3$.

3. Let the amount of $CaCO_3 = x$ g

Let the amount of clay $= y$ g

Thus, $x + y = 5$

On heating, $CaCO_3 \rightarrow CaO + CO_2$

Mass of CO_2 lost $= x \times 44/100$

Clay $\rightarrow$ oxides + water

$$\text{Mass of water lost} = \frac{14.5 \times y}{100}$$

$$\frac{44x}{100} + \frac{14.5 \times y}{100} = 1.507$$

$$x + y = 5.0$$

$$\therefore \quad x = 2.651\ \text{g}$$

$$\text{Or, percentage of } CaCO_3 = \frac{2.651 \times 100}{5} = 53\%.$$

4. (a) Lime for temporary hardness

$Ca(HCO_3)_2 + CaO \rightarrow 2CaCO_3\downarrow + H_2O$

162 parts 56 parts

(b) Soda ash for permanent hardness

$MgCl_2 + Na_2CO_3 \rightarrow MgCO_3\downarrow + 2NaCl$

95 parts 106 parts

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$

136 parts 106 parts

$$\text{Total lime required} = \frac{56 \times 48.6}{102} = 16.8\ \text{ppm}$$

$$\text{Total soda ash required (i)} \quad \frac{106 \times 19.0}{95} = 21.2\ \text{ppm}$$

$$\text{(ii)} \quad \frac{106 \times 68.0}{136} = 53.0\ \text{ppm}$$

Total soda ash required = 21.2 + 53.0 = 74.2 ppm

5. The decomposition on heating of the two compounds follows the reaction:

$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$ and $2NaNO_3 \rightarrow 2NaNO_2 + O_2$

Total moles of O_2 gas which is released

$$= \frac{1}{2}(\text{number of moles of } NaNO_3) + \frac{1}{2}(\text{number of moles of } AgNO_3)$$

$$\text{or} \quad \frac{0.208}{32} = \frac{\text{Moles of } NaNO_3}{2} + \frac{\text{Moles of } AgNO_3}{2}$$

$$\text{or, moles of } NaNO_3 + \text{moles of } AgNO_3 = \frac{2 \times 0.208}{32} = 0.013$$

It is given that the residue completely reacts with 25 mL of N/10 HCl.

$$\text{Therefore, moles of HCl consumed} = 25 \times \frac{1}{10} \times \frac{1}{10^3}$$

$$= 2.5 \times 10^{-3}$$

In the residue, $NaNO_2$ reacts with HCl.

Thus, moles of HCl consumed = Moles of $NaNO_2$ = Moles of $NaNO_3 = 2.5 \times 10^{-3}$

Likewise, moles of $AgNO_3 = 0.013 - 2.5 \times 10^{-3} = 0.0105$

Weight of $AgNO_3 = 0.0105 \times 170 = 1.785$ g or 57.58%

Weight of $NaNO_3 = 2.5 \times 10^{-3} \times 85 = 0.2125$ g or 6.85%

6. (a) With phenolphthalein (first end point)

Let HCl used $= v$ mL

Equivalents of HCl = Equivalents of NaOH + $\frac{1}{2}$ equivalents of Na_2CO_3

$$\frac{1 \times v}{10^3} = \frac{1.1}{40} \times \frac{1}{10^3} + \frac{1}{2} \times \frac{1.1}{53} \times \frac{1}{10^3}$$

Or, $v = 37.88$ mL

Amount of each substance $= \frac{55 \times 20}{1000}$ (since total volume = 1 L)

(b) When methyl orange is added after first end point.

Equivalents of HCl $= \frac{1}{2}$ equivalents of Na_2CO_3 + equivalents of $NaHCO_3$

$$\frac{1 \times v}{10^3} = \frac{1}{2} \times 0.020 \times 10^{-3} + \frac{1.1}{84} \times \frac{1}{1000}$$

In this case, $v = 23.47$ mL

(c) When methyl orange is added from the beginning.

Equivalent of HCl = Equivalents of all

$$\frac{1 \times v}{10^3} = 0.0275 \times 10^{-3} + 2 \times 0.020 \times 10^{-3} + 0.013 \times 10^{-3}$$

Or, $v = 61.35$ mL.

7. Necessary equations:

$KBrO_3 + KI \longrightarrow I_2 + Br^-$

$I_2 + Na_2SO_3 \longrightarrow Na_2S_4O_6 + NaI$

$$\text{Equivalent of } I_2 = \text{Equivalent of } KBrO_3 = \frac{0.334}{167/6} = 12 \times 10^{-3}$$

Equivalent of $Na_2S_2O_3$ = Equivalent of I_2

$$M \times 1 \times \frac{40}{1000} = 12 \times 10^{-3}$$

So, molarity = 0.3 M.

8. Each mole of $K_2Cr_2O_7$ releases 6 moles of electrons which is used by Fe for its reduction.

So, assuming the sample contains x grams of $CuFeS_2$ originally.

$$(\underset{+3}{CuFeS_2} \longrightarrow Fe^{2+} \xrightarrow{K_2Cr_2O_7} Cr^{3+} + Fe^{3+})$$

$$40 \times 0.01 \times 6 = (x/183.5) \times 1000$$

$$x = 0.4404\ \text{g}$$

% of $CuFeS_2$ in sample = (0.4404/0.5) × 100 = 88.08%

9. The equations required are $H_2O + KI + O_3 \longrightarrow I_2 + O_2 + KOH$

Milliequivalents of Iodine = Milliequivalents of KI

= Milli equivalents of O_3 reacted

Milliequivalents of $Na_2S_2O_3 = 1.5 \times 0.01 = 1.5 \times 10^{-2}$

$$\text{Millimoles of Iodine} = \frac{1.5\times10^{-2}}{2} = 7.5\times10^{-3}$$

[∵ 'n' factor for Iodine = 2]

Millimoles of ozone = 7.5×10^{-3}

$$\text{Volume of ozone} = \frac{nRT}{P} = \frac{7.5\times10^{-6}\times0.0821\times300}{1}$$

$$= 184.725 \times 10^{-6} \text{ litre}$$

$$\text{Volume percentage of ozone} = \frac{184.725\times10^{-6}}{10} \times 100$$

$$= 1.847 \times 10^{-3}$$

10. $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

$x/98$

$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$

$1/80$

$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$

According to problem,

Total mass balance, $x + y + 2 = 1$

$$\text{Balancing NaOH} = \frac{23.47}{1000}\times1 = 2\left(\frac{x}{98}+\frac{y}{80}\times\frac{2}{64}\right)$$

Given $z = 0.015$

Solving, we get

$x = 35.36\%$ $\quad y = 63.13\%$ $\quad z = 1.5\%$

Free $SO_3 = 63.13\%$

Combined SO_3 is SO_3 present in H_2SO_4.

$$\Rightarrow \left[\left(\frac{0.3536}{98}\times 80\right)\div 1\right]\times 100 = 28.89\%$$

Single Correct Answer Type

11. (a) $6Cu_3P + 124H^+ + 11Cr2O_7^{2-} \longrightarrow 18Cu^{2+} + 6H_3PO_4 + 22Cr^{3+} + 53H_2O$

12. (c) HNO_3 will also oxidise Fe^{2+}.

13. (c) Meq. of H_2SO_4 + Meq. of SO_3 = Meq. of NaOH

$$\therefore \frac{(0.5-x)}{98/2}\times1000 + \frac{x}{80/2}\times1000 = 26.7\times0.4 \therefore x = 0.103$$

$$\therefore \%\text{ of } SO_3 = \frac{0.103}{0.5}\times 100 = 20.6\%$$

14. (a) Amount of H_2O_2 in one mL $= \frac{34}{1120}$ g

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

∵ 34 g of H_2O_2 gives 16 g or 11200 mL of O_2

$$\therefore \frac{34}{1120} \text{ g of } H_2O_2 = \frac{11200}{34}\times\frac{34}{1120} = 10 \text{ ml of } O_2$$

∴ Volume strength of H_2O_2 = 10 volume

15. (c) Meq. of H_2O_2 = Meq. of I_2

$$\Rightarrow \frac{W_{H_2O_2}}{34}\times2\times1000 = \frac{0.508}{254}\times2\times1000$$

$$\therefore W_{H_2O_2} = 0.06 \text{ g}$$

$$H_2O_2 \longrightarrow H_2O_2 + \frac{1}{2}O_2$$

∵ 34 g H_2O_2 gives 11.2 litres of O_2 at STP

$$\therefore 0.068 \text{ g gives} = \frac{11.2}{34}\times 0.068 = 22.4 \text{ mL of } O_2$$

$$\therefore \text{Volume strength of } H_2O_2 = \frac{22.4}{5} = 4.48 \text{ volume}$$

16. (b) Meq. of H_3PO_4 = Meq. of $Ca(OH)_2$

$\Rightarrow V\times0.25\times2 = 25\times0.03\times2$ (H_3PO_3 is dibasic acid)

$$\therefore V = \frac{25\times3\times2}{25\times2} = 3 \text{ mL}$$

17. (d) At the end point using phenolphthalein as indicator uses complete NaOH and $\frac{1}{2}$ Meq. of Na_2CO_3.

$$\therefore \text{Meq. of NaOH} + \frac{1}{2}\text{ meq. of } Na_2CO_3 = \text{Meq. of HCl}$$

$$\frac{1}{40}\times1000 + \frac{1}{2}\times\frac{1}{106}\times2\times1000 = V\times1$$

$\therefore V = 34.4$ mL

18. (b) $BrO_3^- + 6I^- \longrightarrow 3I_2 + Br^-$

Moles of I_2 = 3 × moles of $KBrO_3$

∴ moles of $I_2 = 0.02 \times 3 = 0.06$

Eq. of I_2 = Eq of Hypo

$0.06 \times 2 = 0.1 \times V$

$V = 1.2$ L = 1200 mL

19. (b) In strong acidic medium, either I produced in reaction tend to be oxidised to I^- or starch used to detect end point is decomposed and hydrolysed.

Multiple Correct Answers Type

20. (b, c)

Meq. of $NaHC_2O_4 = 100 \times 0.1 = 10$

Meq. of NaOH required $= 10 = V_1 \times 0.1 \times 1$

(v.f. of NaOH = 1)

$V_1 = 100$ mL

Meq. of $KMnO_4$ required $= 10 = V_2 \times a \times 5$

(v.f. of $KMnO_4$ = 5)

$$\therefore \quad V_2 = \frac{10}{5a} \qquad \therefore \frac{V_1}{V_2} = \frac{100\times5a}{10}$$

if $M_{KMnO_4} = 0.1$ M, then $10 = V_2 \times 0.1 \times 5$

$\therefore V_2 = 20$ mL

21. (a, b, c)

Meq. of $KMnO_4 = 100 \times 0.1 \times 5 = 50$

= Meq. of $Na_2C_2O_4$ + Meq. of $H_2C_2O_4$

$a + b$

$\therefore \quad a + b = 50$

Meq. of NaOH $= 50 \times 0.2 = 10$ = Meq. of $H_2C_2O_4$

$\therefore \quad b = 10$

$\therefore \quad a = 40$

$$\text{Milli mole of } Na_2C_2O_4 = \frac{a}{2}$$

$$\therefore \text{Milli mole of } C_2O_4 = \frac{a}{2}+\frac{b}{2} = \frac{a+b}{2} = \frac{40+10}{2} = 25$$

$$\text{Milli mole of } H_2C_2O_4 = \frac{b}{2}.$$

22. (a, c, d)

In acidic medium : $Mn^{7+} + 5e \longrightarrow Mn^{2+}$

In neutral medium : $Mn^{7+} + 3e \longrightarrow Mn^{4+}$

In alkaline solution : $Mn^{7+} + e \longrightarrow Mn^{+}$

Note that in alkaline medium, Mn^{6+} is further reduced to Mn^{4+}.

$$Mn^{6+} + 2e \longrightarrow Mn^{4+}$$

Thus, over all reaction may give

$$Mn^{7+} + 3e \longrightarrow Mn^{4+}.$$

23. (a, c, d)

Milli equivalent of $KMnO_4 = 25 \times 0.2 = 5$ meq.

(a) $Fe^{2+} \longrightarrow Fe^{3+}$

Milli equivalent of $FeSO_4 = 25 \times 0.2 \times 1 = 0.2 \times 25 = 5$ (same)

(b) $H_3AsO_3 \longrightarrow H_3AsO_4$

Milli equivalent of $H_3AsO_3 = 2 \times 50 \times 0.1 = 10$ (not same)

(c) $H_2O_2 \longrightarrow 2H^+ + O_2$

Milli equivalent of $H_2O_2 = 25 \times 0.1 \times 2 = 5$ (same)

(d) $Sn^{2+} \longrightarrow Sn^{4+}$

Milli equivalent of $SnCl_2 = 25 \times 0.2 = 25 \times 0.1 = 5$ (same)

24. (a, c)

(a) $6M_1V_1 = M_2V_2$ $\left[\because \text{For } K_2Cr_2O_7, \text{Eq. wt.} = \dfrac{\text{M. wt}}{6}\right]$

(c) $N_1V_1 = N_2V_2$

(b) and (d) are not possible.

25. (a, b, d)

$$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

$$\frac{\text{moles of KI used}}{\text{moles of } KIO_3 \text{ used}} = 5$$

(a) For 0.004 mole KIO_3, moles of KI required $= 0.004 \times 5 = 0.02 = 0.1 \times V_L$

$\therefore V_L = 0.2 \text{ L} = 200 \text{ mL}$

(b) For 0.006 mole H_2SO_4 (0.012 mole H^+), moles of KI required $= \dfrac{0.012 \times 5}{6} = 0.01 = 0.1 \times V_L$

$\therefore V_L = 0.1 \text{ L} = 100 \text{ mL}$

(c) From 0.5 L of KI solution ($n_{KI} = 0.05$), moles of I_2 produced $= \dfrac{0.05 \times 3}{5} = 0.03$

(d) Valency factor of $KIO_3 = 5(\,IO_3^- \longrightarrow I_2)$

$$\therefore \quad E_{KIO_3} = \frac{\text{mol. wt.}}{5}$$

Matching Column Type

26. (a → p, r), (b → q, r), (c → p, q, r), (d → q, r)

(a) Eq. of Sn^{2+} = Moles × v.f. $= 3.5 \times 2 = 7$

Eq. of MnO_4^- = Moles × v.f. $= 1.2 \times 5 = 6$

Since MnO_4^- (O.A) is the LR, so the amount of oxidant available decides the number of electron transfer.

Also, electron involved per mole of OA (5) > electron involved per mole of RA (2).

(b) Eq. of $H_2C_2O_4$ = Moles × v.f. $= 8.4 \times 2 = 16.8$

Eq. of MnO_4^- = Moles × v.f. $= 3.6 \times 5 = 18$

Since $H_2C_2O_4$ (RA) is the LR, so the amount of reductant available decides the number of electron transfer.

Also, electron involved per mole of OA (5) > electron per mole of RA (2)

(c) Eq. of $S_2O_3^{2-}$ = moles × v.f. $= 7.2 \times 1 = 7.2$

Eq. of I_2 = Moles × v.f. $= 3.6 \times 2 = 7.2$.

Since $S_2O_3^{2-}$ (RA) and I_2 (OA) both completely get consumed, so both the amount of reductant and oxidant decides the number of electron transfer.

Also, electron involved per mole of OA (2) > electron involved per mole RA (1)

(d) Eq. of Fe^{2+} = moles × v.f $= 9.2 \times 1 = 9.2$

Eq. of $Cr_2O_7^{2-}$ = moles × v.f $= 1.6 \times 6 = 9.6$.

Since Fe^{2+} (RA) is the LR, so the amount of reductant available decides the number of electron transfer.

Also, electron involved per mole of OA (6) > electron involved per mole RA (1).

Integer Type

27. (5) Step I: To write balanced chemical equation of the redox reaction

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Step II: To calculate the amount of $K_2Cr_2O_7$ required.

It is evident from balanced equation that 1 mole of $Cr_2O_7^{2-} \equiv$ 6 moles of Fe^{2+}.

or 1 mole $K_2Cr_2O_7 \equiv$ 6 moles $FeSO_4$

But 1 mole of $K_2Cr_2O_7 = 2 \times 39 + 2 \times 52 + 16 \times 7 = 294$ g

and 6 moles of $FeSO_4 = 6 \times (56 + 32 + 16 + 4)$

$= 6 \times 152$ g $FeSO_4$

Now 6×152 g of $FeSO_4$ are oxidised by $K_2Cr_2O_7 = 294$ g

$\therefore$ 15.2 g of $FeSO_4$ will require $K_2Cr_2O_7 = \dfrac{294 \times 15.2}{6 \times 152} = 4.9$ g

28. (10) The balanced ionic equation for the reaction is

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

From the balanced equation, it is evident that 1 mole of $KMnO_4$ $\equiv$ 5 moles of $FeSO_4$

Applying molarity equation to the balanced redox equation, we have

$$\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}(FeSO_4)$$

or $\dfrac{1 \times V_1}{8 \times 1} = \dfrac{1}{4} \times \dfrac{25}{5}$ or $V_1 = \dfrac{1 \times 25 \times 8}{4 \times 5} = 10.0 \text{ cm}^3$

Thus, the volume of M/8 $KMnO_4$ solution required = 10.0 mL.

Comprehension Type

29. (a) $\underset{\text{(Bleaching powder)}}{Ca(OCl)Cl} \longrightarrow Ca^{2+} + \overline{O}Cl + Cl^-$

Thus bleaching powder contains OCl^-, i.e. part of oxoacid HOCl and Cl^-, i.e. part of HCl.

Oxidation no. of Cl in oxoacid = +1

Thus, oxide of Cl with same ox. no. is Cl_2O.

$\therefore$ Anhydride of oxoacid (HOCl) is Cl_2O.

30. (c) $CaOCl_2(aq.) + 2KI \longrightarrow I_2 + Ca(OH)_2 + KCl$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

Thus Meq. of $Na_2S_2O_3$ used = Meq. of I_2 formed = Meq. of bleaching powder

or 48×0.25 = Meq. of bleaching powder = $N \times 25$

$\therefore \quad N_{\text{Bleaching powder}} = 0.48$

$\because \quad Cl^+ + 2e \longrightarrow Cl^-$

Thus, n-factor for bleaching powder = 2

$\therefore \quad M_{\text{Bleaching powder}} = \dfrac{0.48}{2} = 0.24.$

DPP 1.7

Subjective Type

1. We have,

$$\text{Eq. mass of oxidant or reductant} = \frac{\text{Molar mass of oxidant or reductant}}{\text{No. of 'e' lost or gained by one molecule of oxidant or reductant}}$$

(a) $\because 2Fe^{2+} \longrightarrow (Fe^{3+})_2 + 2e$

$\therefore$ Eq. mass of $FeSO_4 = \dfrac{\text{Molar mass of } FeSO_4}{1} = \dfrac{152}{1} = 152$

$\because 6e + Cl^{5+} \longrightarrow Cl^-$

$\therefore$ Eq. mass of $KClO_3 = \dfrac{\text{Molar mass of } KClO_3}{6} = \dfrac{122.5}{6}$

$= 20.42$

(b) $\because S^{4+} \longrightarrow S^{6+} + 2e$

$\therefore$ Eq. mass of $Na_2SO_3 = \dfrac{M}{2} = \dfrac{126}{2} = 63$

$\because 3e + Cr^{6+} \longrightarrow Cr^{3+}$

$\therefore$ Eq. mass of $Na_2CrO_4 = \dfrac{M}{3} = \dfrac{162}{3} = 54$

(c) $\because 2(Fe^{(8/3)+})_3 \rightarrow 3Fe_2^{3+} + 2e$

$\therefore$ Eq. mass of $Fe_3O_4 = \dfrac{M}{1} = \dfrac{232}{1} = 232$

$\because 3e + Mn^{7+} \rightarrow Mn^{4+}$

$\therefore$ Eq. mass of $KMnO_4 = \dfrac{M}{3} = \dfrac{158}{3} = 52.67$

(d) $\because 2I^- \rightarrow I_2^0 + 2e$

$\therefore$ Eq. mass of $KI = \dfrac{M}{1} = \dfrac{166}{1} = 166$

$\because 6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$\therefore$ Eq. mass of $K_2Cr_2O_7 = \dfrac{M}{6} = \dfrac{294}{6} = 49$

(e) $\because 2e + Mn^{4+} \longrightarrow Mn^{2+}$

$\therefore$ Eq. mass of $Mn^{4+2} = \dfrac{\text{Atomic mass of Mn}}{2} = \dfrac{52}{2} = 27.5$

(f) $\because 10e + 2N^{5+} \longrightarrow N_2^0$

$\therefore$ Eq. mass of $NO_3^- = \dfrac{\text{Ionic molar mass}}{5} = \dfrac{62}{5} = 12.4$

(g) $\because 6e + N_2^0 \longrightarrow 2N^{3-}$

$\therefore$ Eq. mass of $N_2 = \dfrac{\text{Molar mass of } N_2}{6} = \dfrac{28}{6} = 4.67$

(h) $\because 2S_2^{2+} \rightarrow S_4^{(5/2)+} + 2e$

$\therefore$ Eq. mass of $Na_2S_2O_3 = \dfrac{M}{1} = \dfrac{158}{1} = 158$

$\because 2e + I_2^0 \longrightarrow 2I^-$

$\therefore$ Eq. mass of $I_2 = \dfrac{M}{2} = \dfrac{254}{2} = 127$

(i) $\because FeC_2O_4 \longrightarrow Fe^{3+} + CO_2$

$Fe^{2+} \longrightarrow Fe^{3+} + e$

$C_2^{3+} \longrightarrow 2C^{4+} + 2e$

$FeC_2O_4 \longrightarrow Fe^{3+} + 2C^{4+} + 3e$

$\therefore$ Eq. mass of $FeC_2O_4 = \dfrac{M}{3} = \dfrac{144}{3} = 48$

2. For Sn, $\qquad Sn^{2+} \longrightarrow Sn^{4+} + 2e$

For $Cr_2O_7^{2-}$ $\qquad 6e + C_2^{6+} \rightarrow 2Cr^{3+}$

(a) Meq. of $SnCl_2 = 2000 \times 0.1$

$\therefore \quad \dfrac{w}{E} \times 1000 = 200$

$\therefore \quad \dfrac{w}{189.7/2} \times 1000 = 200 \qquad \left[\because E_{SnCl_2} = \dfrac{M_{SnCl_2}}{2}\right]$

$\therefore \quad w_{SnCl_2} = 18.97$ g

(b) Normality of $K_2Cr_2O_7$

$= \dfrac{4.9}{M/6} \times \dfrac{1}{0.1} = \dfrac{4.9}{294/6 \times 0.1} = 1\text{ N} \qquad \left| N = \dfrac{\text{Eq.}}{\text{litre}} \right.$

3. Redox changes are: $\quad 5e + Mn^{7+} \longrightarrow Mn^{2+}$

$$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$$

$\therefore$ Meq. of oxalate ion

$= \text{Meq. of } KMnO_4 = \dfrac{w}{4} \times 1000 = 90 \times \dfrac{1}{20}$

$\left[E_{C_2O_4^{2-}} = \dfrac{\text{Ionic mass}}{2}\right]$

$\dfrac{w}{88/2} \times 1000 = \dfrac{9}{2}$

$\therefore \quad w_{C_2O_4^{2-}} = 0.198$ g

$\therefore \quad$ 0.3 g $C_2O_4^{2-}$ sample has oxalate ion = 0.198 g

$\therefore \quad$ % of $C_2O_4^{2-}$ in sample $= \dfrac{0.198 \times 100}{0.3} = 66\%$

Single Correct Answer Type

4. (a) $2(Fe^{8/3+})_3 \longrightarrow 3(Fe^{3+})_2 + 2e$

$\therefore \quad E_{Fe_3O_4} = \dfrac{M}{1}$ and $E_{Fe_3O_3} = \dfrac{M}{2/3}$

5. (a) $S^{4+} \longrightarrow S^{6+} + 2e \times 5$

$Mn^{7+} + 5e \longrightarrow Mn^{2+} \times 2$

6. (b) $10e + 2Br^{5+} \longrightarrow (Br^0)_2$

$2Br^- \longrightarrow (Br^0)_2 + 2a$

$2Br^{5+} + 10Br^- \longrightarrow 6Br_2$

6 mole of Br_2 = 2 mole of Br^{5+}

= 10 eq. Br^{5+} = 10 eq. Br_2

$\therefore$ 1 mole $Br_2 = \frac{10}{6}$ eq. $Br_2 = \frac{5}{3}$ eq. Br_2

$\therefore n = \frac{5}{3}$

$\therefore E_{Br_2} = \frac{M}{5/3} = \frac{3M}{5}$.

7. (b) $Mn^{2+} + 5e \longrightarrow Mn^{2+}$

$Fe^{2+} \longrightarrow Fe^{3+} + e$

$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

$[(C^{3+})_2]_3 \longrightarrow 6C^{4+} + 6e$

Eq. of $KMnO_4$ = Eq. of $FeSO_4$ + Eq. of FeC_2O_4 + Eq. of $Fe_2(C_2O_4)_3$

$= 1 \times 1 + 1 \times 3 + 1 \times 6$

$M \times 5 = 10$

$M = 2$

8. (a) Mol. wt. $(CuCO_3) = 63.5 + 12 + 3.16 = 123.5$ g/mol

$$\text{Eq. wt.} (Cu^{2+}\ CO_3^{2-}) = \frac{\text{Molecular weight}}{\text{Valency}} = \frac{123.5}{2}$$

$H_2SO_4 \equiv CuCO_3$

$mEq \equiv mEq$

$$NV\ (mL) = \frac{\text{Weight}}{\text{Equivalent weight}} \times 10^3$$

$$0.5 \times 2\ (n - \text{factor}) \times V = \frac{0.5 \times 10^3}{123.5/2}$$

$$V = \frac{10^3}{123.5} = 8.09 \text{ mL}$$

9. (c) $$\text{Eq. wet.} (NO_3^-) = \frac{m_{wt.}(NO_3^-)}{\text{charge}} = \frac{14 + 3 \times 16}{1} = 62$$

$$\text{Eq. wt.} (SO_4^{2-}) = \frac{m_{wt.}(SO_4^{2-})}{\text{charge}} = \frac{32 \times 4 \times 16}{2} = \frac{96}{2} = 48$$

Equivalent of metal nitrate = Equivalent of metal sulphate

$$= \frac{\text{Weight of metal nitrate}}{\text{Eq. wt. (M)} + \text{Eq. wt.} (NO_3^-)} = \frac{\text{Weight of metal sulphate}}{\text{Eq. wt. (M)} + \text{Eq. wt.} (SO_4^{2-})}$$

$$\Rightarrow \frac{1.0}{E + 62} = \frac{0.86}{E + 48} \qquad \therefore E = 38$$

Multiple Correct Answers Type

10. (a, b, c)

$2Fe^{2+} \longrightarrow (Fe^{3+})_2 + 2e$

$$\text{Eq. mass of } FeS_2 = \frac{M}{22/2} = \frac{M}{11}$$

$2(S^{-1})_2 \longrightarrow 4(S^{4+}) + 20e$

$$\text{Eq. mass of } SO_2 = \frac{M}{20/4} = \frac{M}{5}$$

$\therefore \quad 4e + O_2^0 \longrightarrow 2(O^{2-})$

$\therefore \quad 4\ FeS_2 + 7O_2 \longrightarrow 2Fe_2O_3$

S has –1 oxidation state.

11. (a, b, c)

$(Mn^{7+})_2 + 10e \longrightarrow 2Mn^{2+}$

$Fe^{2+} \longrightarrow Fe^{3+} + e$

$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

$\therefore$ Valence factor for $Ba(MnO_4)$, Fe^{2+}, FeC_2O_4 and $C_2O_4^{2-}$ are 10, 1, 3, 2 respectively.

Meq. of $Ba(MnO_4)_2$ = Meq. of Fe^{2+} = Meq. of FeC_2O_4 = Meq. of $C_2O_4^{2-}$

$$150 \times \frac{1}{10} \times 10 = 150 \times 1 \times 1 = 50 \times 1 \times 3 = 75 \times 1 \times 2$$

12. (a, d)

Cu_2S: $(Cu^+)_2 \longrightarrow 2Cu^{2+} + 2e$

$S^{2-} \longrightarrow S^{6+} + 8e$

$$\therefore \text{Eq. mass of } Cu_2S = \frac{M_1}{10}$$

CuS: Cu^{2+} no change

$S^{2-} \longrightarrow S^{6+} + 8e$

$$\text{Eq. mass of CuS} = \frac{M_2}{8}$$

$Al(MnO_4)_3$: $(Mn^{7+})_3 + 15e \longrightarrow 3Mn^{2+}$

$$\text{Eq. mass of } Al(MnO_4)_3 = \frac{M_3}{15}$$

13. (a, b)

(i) $5e^- + MnO_4^- \to Mn^{2+}$

(ii) $Br_2 \to 2BrO_3^- + 10e^-$

(iii) $2MnO_4^- + Br_2 + 8H^+ \longrightarrow 2Mn^{2+} + 2BrO_4^- + 2H_2O$

$$Ew(MnO_4^-) = \frac{M_1}{5} (n = 5)$$

$$Ew(Br_2) = \frac{M_2}{10} (n = 6)$$

(c) n-factor ratio $(MnO_4^-/Br_2) = \frac{5}{6}$

Matching Column Type

14. (a → p, s), (b → r, s), (c → r), (d → r)

- $As_2S_3 \to As^{5+} + 3SO_4^{2-}$

  n factor = 28

  $\therefore$ Eq. wt. $= \frac{M}{28}$

- $CrI_3 \to \frac{1}{2}Cr_2^{6+} + I^{5+}$

  $\therefore n$ factor = 6 + 15 = 21

  $\therefore$ Eq. wt. $= \frac{M}{21}$

- $CrI_3 \rightarrow \frac{1}{2}Cr_2^{6+} + I^{7+}$

  n factor = 6 + 21 = 27

  $\therefore$ Eq. wt. = $\frac{M}{27}$

- $CrI_3 \rightarrow Cr^{6+} + 3I^{7+}$

  n factor = 6 + 21 = 27

  $\therefore$ Eq. wt. = $\frac{M}{27}$

Integer Type

15. (0.8)

Let M be the molarity of HNO_3 and $Ca(OH)_2$.

$\therefore$ Normality of $HNO_3 = M \times 1 = M$

Meq. of $HNO_3 = 600 \times M$

Meq. of $Ca(OH)_2 = 200 \times 2 \times M = 400\ M$

After reaction, Meq. of acid left = (600 – 400) M = 200 M

Total volume = 600 + 200 = 800 mL

Normality of acid = 200 M/800 = M/4

pH = 1

$\therefore [H^+] = 10^{-1}$

$\therefore M/4 = 10^{-1}$ $\qquad \therefore M = 0.4$

N of $Ca(OH)_2 = 0.4 \times 2 = 0.8$ N

Comprehension Type

16. (a) $\underset{\text{(Bleaching powder)}}{Ca(OCl)Cl} \longrightarrow Ca^{2+} + OCl + Cl^-$

Thus bleaching powder contains OCl^-, i.e., part of oxoacid HOCl and Cl^-, i.e., part of HCl.

Oxidation no. of Cl in oxoacid = +1.

Thus, oxide of Cl with same ox. no. is Cl_2O.

$\therefore$ Anhydride of oxoacid (HOCl) is Cl_2O.

17. (c) $CaCOCl_2(aq.) + 2KI \longrightarrow I_2 + Ca(OH)_2 + KCl$

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

Thus, Meq. of $Na_2S_2O_3$ used = Meq. of I_2 formed = Meq. of bleaching powder

or $\quad 48 \times 0.25$ = Meq. of bleaching powder = N × 25

$\therefore \quad N_{\text{Bleaching powder}} = 0.48$

$\because \quad Cl^+ + 2e \longrightarrow Cl^-$

Thus, n-factor for bleaching powder = 2

$\therefore \quad M_{\text{Bleaching powder}} = \frac{0.48}{2} = 0.24$

CHAPTER 2

DPP 2.1

Subjective Type

1. $N_2H_4 \longrightarrow (Y) + 10e$

$\because$ Y contains all N-atoms

$\therefore \quad (N^{2-})_2 \longrightarrow (2N)^a + 10e$

Therefore, $2a - (-4) = 10$

$a = +3$

2. In a conjugate pair, oxidant has higher oxidation no.

(i) **For $AlCl_3$:** $Al^{3+} + 3e \longrightarrow Al^0$

$\therefore$ **Oxidant is $AlCl_3$**

For K: $K^0 \longrightarrow K^{1+} + e$

$\therefore$ **Reductant is K.**

(ii) **For SO_2:** $S^{4+} + 4e \longrightarrow S^0$

$\therefore$ **SO_2 is oxidant.**

For H_2S: $S^{2-} \longrightarrow S^0 + 2e$

$\therefore$ **H_2S is reductant.**

(iii) No change in ox. no. of either of the conjugate pair.

$\therefore$ **None is oxidant or reductant.**

(iv) **For I_2:** $I_2^0 \longrightarrow 2I^{5+} + 10e$ and $I_2^0 + 2e \longrightarrow 2I^{1-}$

$\therefore$ **I_2 acts as oxidant and reductant both.**

3. **HNO_3:** Ox. no. of N is +5HNO$_3$

Maximum ox. no. of N is +5

Minimum ox. no. of N is –3

Thus, ox. no. of N in HNO_3 is maximum and it can decrease only. That is why HNO_3 acts as oxidant only.

HNO_2: Ox. no. of N is +3 in HNO_2.

Maximum ox. no. of N is +5

Minimum ox. no. of N is –3

Thus, ox. no. of N (in HNO_2) can show an increase or decrease as the case may be. That is why HNO_2 acts as oxidant and reductant both.

4. (a) $Fe_{0.94}O : 0.94 \times a + (-2) = 0$

$$a = \frac{200}{94} = 2.12$$

(b) $Na_2[\mathbf{Fe}(CN)_5NO]$: NO in iron complex has NO^- nature

$\therefore 2 \times 1 + [a + 5 \times (-1) + (+1)] = 0$

$\therefore a = 2$

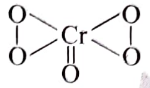
(c) Dimethyl sulphoxide or $(CH_3)_2SO$:

Ox. no. of $CH_3 = +1$; Ox. no. of O = –2

$\therefore 2 \times (+1) + a + (-2) = 0$

$a = 0$

(d) **CrO_5** or **$CrO(O_2)_2$** : CrO_5 has butterfly structure as:



i.e., two peroxide bonds and thus four oxygen atoms have ox. no. = –1 and one oxygen atom has ox. no. –2.

Thus, $a + 4 \times (-1) + 1 \times (-2) = 0 \qquad \therefore a = +6.$

(e) $Ba_2\mathbf{Xe}O_6 : 2 \times 2 + a + 6 \times (-2) = 0$

$a = +8$

(f) C_3O_2: $3 \times a + 2 \times (-2) = 0$

$$\therefore \quad a = +\frac{4}{3}$$

(g) $Ca(\mathbf{ClO_2})_2$: The ClO_2 ion is monovalent and thus for ClO_4^- ions.

$a + 2 \times (-2) = -1 \qquad \therefore a = +3.$

(h) $K[\mathbf{Co}(C_2O_4)_2 . (NH_3)_2]$: $1 + [a + 2 \times (-2) + 2 \times 0] = 0$

$\therefore a = +3$

(i) Na_2S_2: Like peroxide, ox. no. of S in S_2^{2-} is –1.

5. Let the oxidation number of Fe be 'a'.

Fe_3O_4: $3 \times a + 4 \times (-2) = 0$

$$a = +\frac{8}{3}$$

Actually this is average oxidation number of Fe in Fe_3O_4. It exists in FeO . Fe_2O_3 having oxidation number of Fe + 2 in FeO and +3 in Fe_2O_3. Thus, average oxidation number

$$= \frac{2 \times 1 \text{ atom of Fe (in FeO)} + 3 \times 2 \text{ atoms of Fe (in } Fe_2O_3)}{3 \text{ (Total atoms of Fe)}} = +\frac{8}{3}$$

$Fe(III)_4\,[Fe(II)(CN)_6]_3$: Fe(III) has +3 oxidation number

Fe(II) has + 2 oxidation number

Also, average oxidation number $= \dfrac{4 \times (+3) + 3 \times (+2)}{7} = +\dfrac{18}{7}$.

Single Correct Answer Type

6. **(d)** $\underset{+5}{S_2O_6^{2-}} \quad \underset{+6}{S_2O_7^{2-}} \quad \underset{+4}{S_2O_3^{2-}} \quad \underset{0}{S_8}$

$\underset{+6}{H_2SO_4} \quad \underset{+4}{SO_2} \quad \underset{-2}{H_2S} \quad \underset{+6}{H_2S_2O_8}$

$\underset{+6}{SO_2^{2+}} \quad \underset{+6}{SO_4^{2+}} \quad \underset{+4}{SO_3^{2+}} \quad \underset{+6}{HSO_4^-}$

$\underset{+6}{H_2SO_5} \quad \underset{+4}{H_2SO_3} \quad \underset{+2}{S_2Cl_2} \quad \underset{-2}{H_2S}$

7. **(a)** Pr_3O_{11}, $6 \times 9 + (11 \times -2) = 0$ (No O – O bond)

$$a = +\frac{22}{6}$$

8. (c) $\underset{+6}{\underset{\uparrow}{(NH_4)_2Cr_2O_7}} \longrightarrow \underset{+3}{\underset{\uparrow}{Cr_2O_3}}$

9. (a) $\underset{+3}{\underset{\uparrow}{Fe^{III}}}[\underset{+2}{\underset{\uparrow}{Fe^{II}}}\underset{-6}{\underset{\uparrow}{(CN)_6}}]$

10. (d) Each has +7 oxidation state of I.

11. (c) $2 \times 1 + 2[2 \times 1 + a + 2 \times (-2)] = 0$

$a = +1$

12. (b) NH_3 is oxidised to N_2 by O_2. Thus, O_2 is the oxidising agent. In (a), (c) and (d), oxygen is a reducing agent.

13. (b) $\underset{0}{Cu} + \underset{+6}{SO_4^{2-}} \longrightarrow \underset{+2}{Cu^{2+}} + \underset{+4}{SO_2}$

Oxidation

Cu is oxidised by SO_4^{2-}.

Multiple Correct Answers Type

14. (a, b, c, d)

The element (in a molecule) having its oxidation state in the middle (i.e., > minimum and < maximum) can be used as reductant and oxidant both.

15. (a, d)

In nonmetal displacement reactions, a metal or nonmetal displaces another non-metal from its compound.

$$\overset{0}{Cd}(s) + 2\overset{+1}{H}\overset{-1}{Cl}(aq) \xrightarrow{\Delta} \overset{+2}{Cd}\overset{-1}{Cl_2}(aq) + H_2(g)$$

$$\overset{0}{Zn}(s) + 2\overset{+1}{H}\overset{-1}{Cl}(aq) \xrightarrow{\Delta} \overset{+2}{Zn}\overset{-1}{Cl_2}(aq) + \overset{0}{H_2}(g)$$

16. (c, d)

Chlorine can displace $Br^{\ominus}$ and $I^{\ominus}$ ions in an aqueous solution. As Br_2 and I_2 are brown and violet coloured and dissolve in CCl_4, they can easily be identified from the colour of the solution.

$$\overset{0}{Cl_2}(g) + 2Br^{\ominus}(aq) \longrightarrow 2Cl^{\ominus}(aq) + Br_2(l)$$

Orange colour in CCl_4

$$\overset{0}{Cl_2}(g) + 2I^{\ominus}(aq) \longrightarrow 2Cl^{\ominus}(aq) + I_2(s)$$

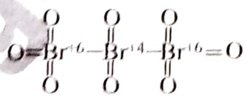
Violet colour in CCl_4

17. (a, b)

Average is zero.

18. (a, b, c)

In Br_3O_8, two Br atoms have +6 oxidation number and one has +4. The average oxidation no. is $+\frac{16}{3}$.



$$O{=}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Br^{+6}}}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Br^{+4}}}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Br^{+6}}}{=}O$$

Matching Column Type

19. (a → q), (b → s), (c → p), (d → r)

- $\underset{-1}{Cl^-} \longrightarrow ClO_4^-$

  $x - 8 = -1$
  $x = +7$
  $+7 - (-1) = 8$

- $\underset{+3}{Cr^{3+}} \longrightarrow CrO_5$

  $x + 4 \times (-1) + 1 \times (-2) = 0$
  $x = +6$
  $+6 - (+3) = 3$

- $H_2O_2 \longrightarrow O_2$

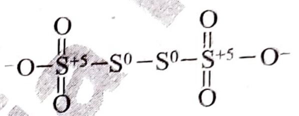
  $2 + 2x = 0$ $\quad$ $2x = 0$
  $2x = -2$
  $0 - (-2) = 2$

- $CrO_2^{2+} \longrightarrow CrO_4^{2-}$

  $x - 4 = +2$ $\quad$ $x - 8 = -2$
  $x = 6$ $\quad$ $x = +6$
  $6 - (+6) = 0$

Integer Type

20. (5)



$$^{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S^{+5}}}{-}S^0{-}S^0{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S^{+5}}}{-}O^{-}$$

21. (3)

$Be_nAl_2Si_6O_{18}$

$Si_6O_{18}^{12-}$ is a cyclic silicate.

$2n + 6 - 12 = 0$

$n = 3$

Comprehension Type

22. (b) $(N^{2-})_2 \longrightarrow N_2^0 + 4e$

$Br^{5+} + 6e \longrightarrow Br$

23. (c) $(N^{2-})_2 \longrightarrow N_2^0 + 4e] \times 3$

$Br^{5+} + 6e \longrightarrow Br^-] \times 2$

24. (a) $(N^{2-})_2 \longrightarrow N_2^0 + 4e] \times 3$

$Br^{5+} + 6e \longrightarrow Br^-] \times 2$

$3N_2H_4 + 2BrO_3^- \longrightarrow 3N_2 + 2Br^-$

Balancing H atoms

$3N_2H_4 + 2BrO_3^- \longrightarrow 3N_2 + 2Br^- + 6H_2O$

25. (a) BrO_3^- acts as an oxidant and N_2H_4 as reductant.

26. (a) BrO_3^- as oxidant and its conjugate reductant is Br^-.

27. (a) It is intermolecular redox where one species is oxidised and the other is reduced.

DPP 2.2

Subjective Type

1. Total charge on LHS = Total charge on RHS.

$(-1) + 8 + (-n) = +2$

$\therefore n = 5.$

2. (a) $BaCrO_4 + KI + HCl \longrightarrow BaCl_2 + I_2 + KCl + CrCl_3 + H_2O$

Step I. $3e + Cr^{6+} \longrightarrow Cr^{3+}$

$2I^- \longrightarrow I_2 + 2e$

Step II. $6e + 2Cr^{6+} \longrightarrow 2Cr^{3+}$

$$\begin{array}{l} 6I^- \longrightarrow 2I_2 + 6e \\ \hline 2Cr^{6+} + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 \end{array}$$

Step III. $2BaCrO_4 + 6KI \longrightarrow CrCl_3 + 3I_2$

Step IV. Balancing of other atoms except (H and O), i.e. Ba, K and Cl.

$2BaCrO_4 + 6KI + 16HCl \longrightarrow 2CrCl_3 + 3I_2 + 6KCl + 2BaCl_2$

Step V. Balance H-atom

$2BaCrO_4 + 6KI + 16HCl \longrightarrow 2CrCl_3 + 3I_2 + 6HCl + 2BaCl_2 + 8H_2O$

(b) $SO_2 + Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2SO_4 + Cr_2(SO_4)_3 + H_2O$

Step I. $S^{4+} \longrightarrow S^6 + 2e$

$6e + 2Cr^{6+} \longrightarrow (Cr^{3+})_2$

Step II. $3S^{4+} \longrightarrow 3S^{6+} + 6e$

$$\begin{array}{l} 6e + 2Cr^{6+} \longrightarrow (Cr^{3+})_2 \\ \hline 3S^{4+} + 2Cr^{6+} \longrightarrow 3S^{6+} + (Cr^{3+})_2 \end{array}$$

Three S^{6+} atoms are distributed in $2Na_2SO_4$ and $1Cr_2(SO_4)_3$

Step III. $3SO_2 + 2Na_2CrO_4 \longrightarrow 2Na_2SO_4 + Cr_2(SO_4)_3$

Balancing of other atoms, i.e., S in SO_4.

Step IV. $3SO_2 + 2Na_2CrO_4 + 2H_2SO_4 \longrightarrow 2Na_2SO_4 + Cr_2(SO_4)_3$

Step V. Balancing H-atom

$3SO_2 + 2Na_2CrO_4 + 2H_2SO_4 \longrightarrow 2Na_2SO_4 + Cr_2(SO_4)_3 + 2H_2O$

3. Cl_2 can undergo only in Cl^- state to show loss of electron. Since loss and gain of 14 electrons occur between Cl_2 and thus 7 mole show oxidation.

$Cl_2 + 2e \longrightarrow 2Cl^-] \times 7$

$$\begin{array}{l} Cl_2^0 \longrightarrow 2Cl^{7+} + 14e \\ \hline 8Cl_2 \longrightarrow 2Cl^{2+} + 14Cl^- \end{array}$$

4. Disproportionate reaction

$\underset{\substack{x-6=-1 \\ x=5}}{ClO_3^-} \longrightarrow \underset{\substack{x-8=-1 \\ x=7}}{ClO_4^-} + 2e^-$ $(x = 2)$ (Oxidation)

$e^- + \underset{x=5}{ClO_3^-} \longrightarrow \underset{\substack{x-4=0 \\ x=4}}{ClO_2}$ $(x = 1)$ (reduction)

$E_w = M + \frac{M}{2}$.

Single Correct Answer Type

5. (c) $\underset{\substack{\uparrow \\ p}}{Br_2} + \underset{\substack{\uparrow \\ q}}{6OH^-} \longrightarrow \underset{\substack{\uparrow \\ r}}{5Br^-} + \underset{\substack{\uparrow \\ s}}{BrO_3^-} + \underset{\substack{\uparrow \\ t}}{3H_2O}$

Br_2 disproportionates to BrO_3^- when treated with hot alkali solution.

$\frac{1}{2}Br_2 + e^- \longrightarrow Br^-] \times 5$

$$\begin{array}{l} \frac{1}{2}Br_2 + 6OH^- \longrightarrow BrO_3^- + 3H_2O + 5e^- \\ \hline 3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O \\ \hline \end{array}$$

6. (c) $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$

I^- and I_2 are not balanced.

7. (b) CuS (black ppt) on boiling with HNO_3 results in the formation of colloidal S and blue coloured solution of $Cu(NO_3)_2$.

8. (c) Let sulphur be as $(S_n)^x$.

x = charge
n = number of sulphur atoms

$(S_n)^x + 12OH^- \longrightarrow 4S^{2-} + 2S_2O_3^{2-} + 3H_2O$

Charge-balanced: $x + (-12) = -8 - 4$

$\therefore \quad x = 0$

Sulphur-balanced: $x = 4 + 4$

$\therefore \quad S = 8$

Thus, (S_8).

9. (d) $CN^- \longrightarrow CNO^-$

O.N. of nitrogen $4 + x = -1$ $\qquad 4 + x - 2 = -1$

$x = -5 \qquad x = -3$

CN^- is thus oxidised. Thus, two electrons are lost.

10. (c) $As_2S_3 \longrightarrow AsO_4^{3-} + 3SO_4^{2-}$

$$\begin{array}{llll} \text{O.N.} & 2As = +6 & 2 \times 5 & 3 \times 6 \\ & 3s = -6 & = 10 & = 18 \end{array}$$

Net = –Total = 28 Net change = 28

Thus, equivalent mass of $As_2O_3 = \frac{M}{28}$

11. (d) $\underset{\substack{\uparrow \\ +5}}{Cu_3P} \longrightarrow \underset{\substack{\uparrow \\ +5}}{H_3PO_4}$

Change in oxidation number = 8 units of phosphorus

$\therefore$ Equivalent weight of $H_3PO_4 = \frac{M}{8}$

Multiple Correct Answers Type

12. (a, b, c)

$E_{wt.} = \frac{M_{wt.}}{n}$

- $MnO_4^- + 5e^+ \longrightarrow Mn^{2+} + 4H_2O$ $(n = 5)$ (acidic medium)
- $e^- + MnO_4^- \longrightarrow MnO_4^{2-}$ $(n = 1)$ (basic medium)
- $3e^- + MnO_4^- + 4H^+ \longrightarrow MnO_2 + 2H_2O$ $(n = 3)$ (neutral medium or dilute basic solution)

13. (a, b, c)

- As an acid:

  $HC_2O_4^- \longrightarrow H^+$ $(n=1)$

- As reducing agent

  $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ $(n = 2)$

- $Ca(HC_2O_4)_2$ can be estimated by MnO_4^-/H^+.

14. (a, c, d)

Br_2 disproportionates (simultaneous oxidation and reduction), its equivalent weight is the sum of equivalent weights of the two half reactions.

$$2e^- + Br_2 \longrightarrow 2Br^- \ (x = 2) \qquad \text{reduction}$$

$$\underset{2x=0}{Br_2} \longrightarrow \underset{\substack{2x-12=-2\\ 2x=+10}}{2BrO_3^-} + 10e^- \ (x = 10) \qquad \text{oxidation}$$

$$\therefore E_{wt.} = \frac{M}{2} + \frac{M}{10} = \frac{160}{2} + \frac{160}{10}$$

$$= 80 + 16 = 96$$

15. (a, c)

Hg gets oxidised by O_3 to give sticking nature on glass.

$$2Hg + O_3 \longrightarrow Hg_2O + O_2$$

$$Hg_2O + H_2O_2 \longrightarrow Hg_2 + H_2O + O_2$$

16. (a, b, d)

$$6e + Cl^{5+} \longrightarrow Cl^-$$

$$2I^- \longrightarrow I_2 + 2e$$

On balancing, we get the balanced equation as

$$\underset{\text{Oxidation}}{ClO_3^-} + \underset{\text{Reduction}}{6I^-} + 6H_2SO_4 \longrightarrow 3I_2 + Cl^- + 6HSO_4^- + 3H_2O$$

Matching Column Type

17. (a → (i) → q), (b → (ii) → p), (c → (ii) → r), (d → (iii) → s)

CH_4: $C^{-4} \longrightarrow C^{4+}$ $(n = 8)$ (E. mass = M/8)

CO: $C^{2+} \longrightarrow C^{4+}$ $(n = 2)$ (E. mass = M/2)

$C_2O_4^{2-}$: $2C^{3+} \longrightarrow 2C^{4+}$ $(n = 2)$ (E. mass = M/2)

C_2H_4: $2C^{-2} \longrightarrow 2C^{4+}$ $(n = 12)$ (E. mass = M/12)

Integer Type

18. (5)

Balanced equation is

$$2CrSCN^{2+} + 19BrO^- + 18OH^- \longrightarrow 19Br^- + 2NO_3^- + 2CO_3^{2-} + 2SO_4^{2-} + 2CrO_4^{2-} + 9H_2O$$

Thus, five species have coefficient equal to 2.

19. (7)

$$14e^- + 2NO_3^- + 16H^+ \longrightarrow N_2H_4 + 6H_2O$$

Thus, one mole of NO_3^- ion will require 7 mol of electrons.

Comprehension Type

20. (b) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

21. (c) $4NaCl + K_2Cr_2O_7 + 6H_2O_4 \longrightarrow 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O$

22. (a) $CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O$

$CrO_3 + 2NaOH \longrightarrow Na_2CrO_4 + H_2O$

23. (a) $[Sn^{2+} \longrightarrow Sn^{4+} + 2e] \times 3$

$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

∴ 1 mole of $K_2Cr_2O_7$ will oxidise 3 mole of Sn^{2+}.

CHAPTER 3

DPP 3.1

Subjective Type

1. In the formation of Zn^{2+} from Zn, two electrons are removed. The number of protons and neutrons remains unchanged. Hence, the atomic weight of Zn^{2+} will be 70.

2. Total number of molecules of $CO_2 = 12$

Types of molecules	Molecular weight
1. $C^{12}O^{16}O^{16}$	44
2. $C^{12}O^{17}O^{17}$	46
3. $C^{12}O^{18}O^{18}$	48
4. $C^{12}O^{16}O^{17}$	45
5. $C^{12}O^{16}O^{18}$	46
6. $C^{12}O^{18}O^{18}$	47

Similarly, six molecules with C^{13} isotopes can be found.

3. Wavelength (λ) of radiation = 580 nm = 580×10^{-9} m
$= 5.80 \times 10^{-7}$ m
Velocity of radiation $c = 3 \times 10^8$ m s^{-1}
$c = \nu\lambda$

$$\text{Frequency } \nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ms}^{-1}}{5.80 \times 10^{-7}\text{m}} = 5.17 \times 10^{14}\text{s}^{-1}$$

$$\text{Wavenumber } \overline{\nu} = \frac{1}{\lambda} = \frac{1}{5.80 \times 10^{-7}\text{m}} = 1.72 \times 10^6 \text{m}^{-1}$$

4. Energy emitted by sodium lamp in 1 s.
= Watt × second = 60 × 1 J

$$\text{Energy of photon emitted} = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{5893 \times 10^{-10}} = 3.37 \times 10^{-19} \text{ J}$$

$$\therefore \text{Number of photons emitted per second} = \frac{60}{3.37 \times 10^{-19}}$$

∴ Number of photons emitted in 10 hours
$= 6.41 \times 10^{24}$
$= 17.8 \times 10^{19} \times 10 \times 60 \times 60$

5. Using Einstein's photoelectron equation,

$$KE = h\nu - h\nu_0 = h(\nu - \nu_0)$$
$$KE_1 = h(\nu_1 - \nu_0) \quad \text{(i)}$$
$$KE_2 = h(\nu_2 - \nu_0) \quad \text{(ii)}$$

Dividing equation (ii) by (i), we get

$$\frac{KE_2}{KE_1} = 3$$

$$\therefore \quad 3 = \frac{\nu_2 - \nu_0}{\nu_1 - \nu_0} \Rightarrow 3(\nu_1 - \nu_0) = \nu_2 - \nu_0$$

$$\Rightarrow \quad 3\nu_1 - \nu_2 = 3\nu_0 - \nu_0 = 2\nu_0$$

$$\Rightarrow \quad 3 \times 2.0 \times 10^{16} - 4 \times 4 \times 10^{16} = 2\nu_0$$

$$\Rightarrow \quad \nu_0 = \frac{2 \times 10^{16}}{2} = 1 \times 10^{16}\text{s}^{-1}$$

6. $q = ne$

$$n = \frac{q}{e} = \frac{+1.282 \times 10^{-18}}{+1.6 \times 10^{-19}}$$
$$= 8.01 \approx 8$$

7. % of α-particles sent back

$$= \frac{1}{20000} \times 100$$
$$= 5 \times 10^{-3}$$

So $x = 3$.

8. $R_{\text{Al-nucleus}} = 1.4 \times 10^{-15} \times A^{1/3}$
$= 1.4 \times 10^{-15} \times (27)^3$ m
$= 4.2 \times 10^{-15}$ m
So $x = 4.2 \approx 4$

Single Correct Answer Type

9. (a) M_1 = Atomic weight $\quad Z_1$ = Atomic number
In isobars $M_1 = M_2$ and in isotopes $Z_1 = Z_2$.
In isotones (isoneutronic elements) $M_1 - Z_1 = M_2 - Z_2$

10. (c) $\sqrt{\nu} = a(Z - b)$

11. (d) When intensity is doubled, the number of electrons emitted per second is also doubled, but the average energy of photoelectrons emitted remains the same.

12. (d) $N(\theta) \propto \dfrac{1}{K.E^2}$

Inversely proportional to $K.E^2$.

13. (c) Energy of the incident radiation = Work function + Kinetic energy of photoelectron

Energy of incident radiation (E)

$$= h\nu = h\frac{c}{\lambda} = \frac{(6.626 \times 10^{-34}\text{Js})(3.0 \times 10^8 \text{ms}^{-1})}{(256.7 \times 10^{-9}\text{m})}$$

$= 7.74 \times 10^{-19}$ J = 4.83 eV (1 eV = 1.602×10^{-19} J)

The potential applied gives the kinetic energy to the electron. Hence, kinetic energy of the electron = 0.35 eV

∴ Work function = 4.83 eV – 0.35 eV = 4.48 eV

14. (a) $$\frac{V_{\text{nucleus}}}{V_{\text{atom}}} = \frac{\frac{4}{3}\pi r_1^3}{\frac{4}{3}\pi r_2^3} = \left(\frac{1.5 \times 10^{-15}}{0.5 \times 10^{-10}}\right)^3 = 2.7 \times 10^{-14}$$

15. (a) $E = \dfrac{hc}{\lambda} \times N_A$

$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 6.022 \times 10^{23}}{5000 \times 10^{-10}} \text{J/mol}$$

$= 239.4$ kJ/mol

≈ 240 kJ mol^{-1}

Multiple Correct Answers Type

16. (a, d)

Scattering is due to coulombic forces and it follows hyperbolic path.

17. (a, b, c)

Elastic collision of electron with metal surface is not possible.

18. (a, b, c, d)

19. (a, b, d)

$$E = \frac{h\nu}{c} \quad E \propto \nu, E \propto \bar{\nu}$$

$$\because \quad \bar{\nu} = \frac{1}{\lambda},$$

$$E \propto h\nu$$

20. (a, b, c, d)

$10 \text{ cm}^{-1} = 1000 \text{ m}^{-1}$

$$\therefore \quad E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

$= 6.66 \times 10^{-34} \text{ (Js)} \times 3 \times 10^{8} \text{ (ms}^{-1}) \times 1000 \text{ (m}^{-1})$

$= 2 \times 10^{-22}$ J per photon $= 2 \times 10^{-15}$ ergs per photon

$= 2 \times 10^{-22} \times 6.02 \times 10^{23} \text{ J mol}^{-1}$

$= 1.2 \times 10^{-1} \text{ kJ mol}^{-1}$

$= 2.9 \times 10^{-2} \text{ kcal mol}^{-1}$

Matching Column Type

21. (a → q), (b → r), (c → t), (d → p), (e → s)

Integer Type

22. (5) Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$h\frac{c}{\lambda} = E_0 + 1 \text{ eV} \qquad \text{(i)}$$

$$3h\frac{c}{\lambda} = E_0 + 4 \text{ eV} \qquad \text{(ii)}$$

$3(E_0 + 1 \text{ eV}) = E_0 + 4 \text{ eV}$

$E_0 = 0.5 \text{ eV} = 5 \times 10^{-1} \text{ eV} \quad \Rightarrow x$ is 5

Comprehension Type

23. (d) i.e. $V_0 = \dfrac{h(\nu - \nu_0)}{e}$

24. (b) It is clear from the given figure.

25. (d) $\Delta E_{2E \to E} = E - 2E = \dfrac{hc}{\lambda} \Rightarrow hc = -\lambda E \qquad (1)$

$$\Delta E_{\frac{4E}{3} \to E} = E - \frac{4E}{3} = \frac{hc}{\lambda}$$

$$\Rightarrow \quad \frac{-E}{3} = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{-hc \times 3}{E}$$

$$\Rightarrow \quad \lambda = \frac{(-1) \times (-\lambda E)}{E} \times 3 = 3\lambda$$

26. (c)

K.E. of emitted doesn't depend on intensity. It depends on frequency of incident radiation.

DPP 3.2

Subjective Type

1. For the first line in Balmer series, $n_1 = 2$ and $n_2 = 3$. So

$$\bar{\nu} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$= 109677\left[\frac{1}{(2)^2} - \frac{1}{(3)^2}\right]\text{cm}^{-1}$$

$$= 109677 \times \frac{5}{36} \text{ cm}^{-1}$$

$$= 15232.9 \text{ cm}^{-1}$$

$$\text{or} \quad \lambda = \frac{1}{\bar{\nu}} = \frac{1}{15{,}232.9}\text{cm} = 6.565 \times 10^{-5} \text{ cm} = 656.5 \text{ nm}$$

2. For Li^{2+}, transition occurs from n_1 = to $n_2 = 3$.

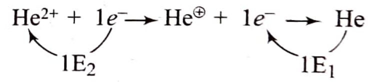
$$\therefore \quad \bar{\nu} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad [\text{for } Li^{2+}, Z = 3]$$

$$\bar{\nu} = 109677 \times 3^2\left[\frac{1}{1^2} - \frac{1}{3^2}\right]$$

$$\bar{\nu} = 8.77 \times 10^{7} \text{ m}^{-1}$$

$$\text{or} \quad \lambda = \frac{1}{\bar{\nu}} = 113.9 \text{ Å}$$

3.



$$He^{2+} + 1e^- \longrightarrow He^{\oplus} + 1e^- \longrightarrow He$$

IE = ionization energy of He

$IE_1 = 3.4 \times 10^{-19}$ J

IE_2 = IE of He^+ ion as IE of H like atom $= IE_{H\text{ atom}} \times Z^2$ and $= IE_{H\text{ atom}} = E_\infty - E_1 = 0 - (-2.17 \times 10^{-18}) \text{ J} = 2.17 \times 10^{-18}$ J

$= 2.17 \times 10^{-18} \times (4) = 8.68 \times 10^{-18}$ J

Total energy required to make He^{2+}

$IE_1 + IE_2 = (3.4 \times 10^{-19} + 8.68 \times 10^{-18})$ J

$= 90.2 \times 10^{-19} = 9.02 \times 10^{-18}$ J

Thus energy released when He^{2+} is converted back to He is 9.02×10^{-18} J.

4. According to Bohr's model,

$$mvr = \frac{nh}{2\pi}; \text{ Given } n = 1 \text{ and } 2\pi r \text{ (circumference)}$$

$$= 3.322 \times 10^{-10} \text{ m}$$

$$v = \frac{nh}{2\pi mr} = \frac{1 \times (6.626 \times 10^{-34} \text{ Js})}{(9.1 \times 10^{-31} \text{ kg}) \times 3.322 \times 101^{-10} \text{ m}}$$

$$= 2.19 \times 10^{6} \text{ m s}^{-1}$$

5. (a) $16.52 = (E_3 - E_2) \times Z^2$

$16.52 = 1.89 \times Z^2 \Rightarrow Z^2 = 9$ or $Z = 3$

(b) $(E_3 - E_1)_Z = 12.09 \times Z^2 = 12.09 \times 9 = 108.81$ eV

(c) $\lambda = \dfrac{12400}{\Delta E_{1\to\infty}} = \dfrac{12400}{13.6 \times 3^2} = 101.3$ Å $= 1.013 \times 10^{-8}$ m.

(d) $KE_1 = 13.6\, Z^2$ eV $= 13.6 \times 3^2 = 122.4$ eV

6. Total no. of transition $= \dfrac{n(n-1)}{2} = 6$

$\Rightarrow n = 4$

So He$^+$ ion has its e^- in 4th orbit.

So its separation energy

$$E_{He^+} = 13.6 \times \frac{Z^2}{n^2} = 13.6 \times \frac{4}{16} \text{ eV}$$

$$\Rightarrow \quad E_{He^+} = \frac{13.6}{4} \text{ eV} \qquad \text{(i)}$$

Ionisation energy of Hydrogen,

$E_H = 13.6$ eV

So $\quad E_H / E_{He^+} = 4 \qquad$ (ii)

7. Let separation energy of ion = E, then

$$E = 13.6 \times Z^2 \times \frac{1}{16} \text{ eV}$$

and $E_H = 13.6 \times \dfrac{1}{4}$ eV

$$\Rightarrow \quad \frac{E}{E_H} = Z^2 \times \frac{4}{16}$$

$$\Rightarrow \quad \frac{2.25\, E_H}{E_H} = \frac{Z^2}{4} \Rightarrow Z^2 = 9 \Rightarrow Z = 3$$

8. For line (1), the photon emitted by electronic transition ($n = 4$ to $n = 2$) in He$^+$ ion will cause the electron in H-atom to make a transition for $n = 1$ to $n = 2$, because

$$\underbrace{13.6(2)^2\left[\frac{1}{2^2} - \frac{1}{4^2}\right]}_{\substack{\text{Energy of photon emitted}\\ \text{in transition } n=4 \text{ to } n=2\\ \text{in He}^+ \text{ ion}}} = \underbrace{13.6(1)^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right]}_{\substack{\text{Energy of photon required}\\ \text{for transition } n=1 \text{ to } n=2\\ \text{in H-atom}}}$$

Thus, wavelength of photon emitted by H-atom when it returns from $n = 2$ to $n = 1$ will be

$$\lambda = \frac{12400}{13.6\left[1 - \frac{1}{4}\right]} = \frac{12400}{10.2} \approx 1216 \text{ Å}$$

For line (2), the photon emitted by electronic transition ($n = 6$ to $n = 2$), in He$^+$ ion will cause the electron in H-atom to make a transition from $n = 1$ to $n = 3$, because

$$\underbrace{13.6(2)^2\left[\frac{1}{2^2} - \frac{1}{6^2}\right]}_{\substack{\text{Energy of photon emitted}\\ \text{in transition } n=6 \text{ to } n=2\\ \text{in He}^+ \text{ ion}}} = \underbrace{13.6(1)^2\left[\frac{1}{1^2} - \frac{1}{3^2}\right]}_{\substack{\text{Energy of photon required}\\ \text{for transition } n=1 \text{ to } n=3\\ \text{in H-atom}}}$$

Thus, wavelength of photon emitted by H-atom when it returns from $n = 3$ to $n = 1$ will be:

$$\lambda_1 \text{ (Corresponding to } 3 \to 2 \text{ transition)} = \frac{12400}{13.6\left[\frac{1}{4} - \frac{1}{9}\right]}$$

$$\approx 6565 \text{ Å}$$

$$\lambda_2 \text{ (Corresponding to } 2 \to 1 \text{ transition)} = \frac{12400}{13.6\left[1 - \frac{1}{4}\right]}$$

$$\approx 1216 \text{ Å}$$

(already emitted from line (1))

$$\lambda_3 \text{ (Corresponding to } 3 \to 1 \text{ transition)} = \frac{12400}{13.6\left[1 - \frac{1}{9}\right]}$$

$$\approx 1026 \text{ Å}$$

For line (3), the electronic transition from $n = 4$ to $n = 3$ in He$^+$ ion will not cause any transition in H-atom sample. Consequently, no photons will be emitted.

Similarly, for line (4), the electronic transition from $n = 3$ to $n = 2$ in He$^+$ ion will not cause any transition in H-atom sample. Consequently, not photons will be emitted.

Thus, the wavelengths of the photons subsequently emitted by H-atoms will be

$\lambda_{3\to2} = 6565$ Å, $\lambda_{2\to1} = 1216$Å, $\lambda_{3\to1} = 1026$ Å

Single Correct Answer Type

9. (a) $\dfrac{1}{\lambda} = R\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

For Balmer series, $n_1 = 2$

For fourth line, $n_2 = 4 + 2 = 6$

For fifth line, $n_2 = 5 + 2 = 7$

$$\frac{1}{\lambda_4} = R\left[\frac{1}{4} - \frac{1}{36}\right]$$

$$\Rightarrow \quad \lambda_4 = \frac{36}{8R} = \frac{4.5}{R}$$

$$\frac{1}{\lambda_5} = R\left[\frac{1}{4} - \frac{1}{49}\right] = R\left[\frac{49-4}{4 \times 49}\right] = \frac{R \times 45}{4 \times 49} \Rightarrow \lambda_5 = \frac{4 \times 49}{45 \times R}$$

$$\lambda_5 = \frac{4.35}{R} \Rightarrow \lambda_4 - \lambda_5 = \frac{4.5}{R} - \frac{4.356}{R} = \frac{0.1444}{10977} \times 10^{-8} \text{ Å} = 131 \text{ Å}$$

10. (d) $T^2 \propto r^3$

$$\frac{T_r}{R_{4r}} = \left(\frac{r}{4r}\right)^{3/2} = \frac{1}{8}$$

11. (a) As $V = 3.185 \times 10^8 \times \dfrac{Z}{n}$ cm s^{-1}. So, $V \propto Z$, $V \propto \dfrac{1}{n}$.

12. (b) Radius ratio of K and L shell = 1 : 4

Energy difference = −3.4 − (−13.6) = 10.2 eV

Radius ratio of level L and N shell = 2 : 4

= −0.85 − (−3.4)

= 2.55 eV

13. (b)

$$E_1(\text{H}) = -13.6 \times \frac{1^2}{1^2} = -13.6 \text{ eV};$$

$$E_2(\text{He}^+) = -13.6 \times \frac{2^2}{2^2} = -13.6 \text{ eV}$$

$$E_3(\text{Li}^{2+}) = -13.6 \times \frac{3^2}{3^2} = -13.6 \text{ eV};$$

$$E_4(\text{Be}^{3+}) = -13.6 \times \frac{4^2}{4^2} = -13.6 \text{ eV}$$

$$\therefore E_1(\text{H}) = E_2(\text{He}^+) = E_3(\text{Li}^{2+}) = E_4(\text{Be}^{3+})$$

14. (a) $r_1 - r_2 = 24 \times (r_1)_\text{H}$

$$\frac{0.529 \times n_1^2}{1} - \frac{0.529 \times n_2^2}{1} = 24 \times 0.529$$

$$\therefore \quad (n_1^2 - n_2^2) = 24$$

So, $n_1 = 5$ and $n_2 = 1$.

15. (d) According to energy, $E_{4\to1} > E_{3\to1} > E_{2\to1} > E_{3\to2}$

According to energy, Violet > Blue > Green > Red.

$\therefore$ Red line $\Rightarrow 3 \to 2$ transition.

Multiple Correct Answers Type

16. (a, d)

$$E_3 = E_1 + E_2$$

$$h\nu_3 = h\nu_1 + h\nu_2$$

$$\nu_3 = \nu_1 + \nu_2$$

$$\frac{c}{\lambda_3} = \frac{c}{\lambda_1} + \frac{c}{\lambda_2}$$

$$\frac{1}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\lambda_3 = \frac{\lambda_1\lambda_2}{\lambda_1 + \lambda_2}$$

17. (c, d)

$$\text{I.E.} = +\frac{2\pi^2 mz^2e^4}{n^2h^2}$$

When mass becomes double, the ionization energy will be doubled.

18. (b, c)

$$\upsilon = \frac{2.188 \times 10^8}{n} \text{cm/sec}$$

$$r = n^2 \times 0.529 \times 10^{-8} \text{ cm}$$

$$E = -\frac{2.18 \times 10^{-18}}{n^2}$$

These relations show that υr and $\frac{\upsilon}{E}$ will be proportional to the principal quantum number n.

19. (a, d)

$$r = \frac{n^2}{Z} \times 0.529 \text{ Å}$$

Here, radius is inversely proportional to atomic number Z.

$$E = -\frac{Z^2}{n^2} \times 2.18 \times 10^{-18} \text{ J}$$

$E \propto Z^2$, here –ve signifies the release of energy when the electron comes nearer to the nucleus.

20. (a, d)

$$T_n = \frac{2\pi r_n}{\upsilon_n}$$

$$T_n \propto \frac{r_n}{\upsilon_n}, \quad r_n \propto n^2, \quad \upsilon_n \propto \frac{1}{n} \quad \therefore T_n \propto n^3$$

$$\text{Here, } 8 = \left(\frac{n_1}{n_2}\right)^3$$

$$n_1 = 2n_2$$

21. (a, c)

Option A $\text{E}_{\text{H}(n=4)} = -13.6 \times \frac{1}{16} \text{ eV} = -0.85 \text{ eV}$

$\text{E}_{\text{He}^+(n=4)} = -13.6 \times \frac{1}{16} \text{ eV} = -3.4 \text{ eV}$

So $\quad -0.85 > -3.4$

$\Rightarrow \quad \text{E}_{\text{H}(n=4)} > \text{E}_{\text{He}^+(n=4)}$

Option C $\text{E} = \frac{h}{\lambda} \Rightarrow \text{E} \propto \frac{1}{\lambda}$

22. (a, c)

Ground state binding energy = $13.6\,Z^2 = 122.4$ eV.

$\therefore Z = 3$.

1st excitation energy = $10.2\,Z^2 = 91.8$ eV.

$\therefore$ An 80 eV electron cannot excite it to a higher state.

Matching Column Type

23. (a → q, r, s)

$n_1 \to n_\infty$ in H atoms:

- UV region (Lyman series)
- $\Delta E = \frac{hc}{\lambda} = hcR \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = \text{h}cR$ (Rydberg energy)
- Ionisation energy

(b → p)

$n_4 \to n_2$ in $\text{He}^\oplus$ ion:

- UV region (check yourself)

(c → r, s)

$n_\infty \to n_1$ in $\text{He}^\oplus$ ion:

- UV region (check yourself)
- Corresponding to Ionisation energy

(d → p)

$n_4 \to n_2$ in ion

- Visible region (Balmer series)

Integer Type

24. (3) $\text{IE}_{\text{H like atom}} = \text{IE}_{\text{H atom}} \times \text{Z}^2$

$$\text{Z}^2 = \frac{11180}{1312} = 8.521$$

$$\Rightarrow \quad \sqrt{8.521} = \text{Z}$$

$$\text{Z} = 2.917 \approx 3$$

25. (3) 5 → 2

4 → 2

3 → 2

Coming back to $n = 2$ is in visible region.

26. (2) Radius of ground state of hydrogen atom = 0.529 Å

$$0.529 = 0.529 \times \frac{n^2}{\text{Z}}$$

$$0.529 = 0.529 \times \frac{n^2}{4}$$

$$\therefore n = 2$$

Comprehension Type

27. (d)

$$\text{Attractive force} = \frac{2KZe^2}{r^2} = \text{repulsion force}$$

$$= \frac{2m_e v_1^2}{r}$$

$$\therefore \quad \frac{2KZe^2}{r_1^2} = \frac{2m_e v_1^2}{r_1}$$

$$\text{or} \quad r_1 = \frac{KZe^2}{m_e v_1^2}$$

In the Bohr orbit, $m v_1 r_1 = \dfrac{nh}{2\pi}$

$$\text{or} \quad v_1 = \frac{nh}{2\pi m r_1}$$

$$\therefore \quad r_1 = \frac{KZe^2}{m_e \times \dfrac{n^2 \times h^2}{4\pi^2 \times 4m_e^2 \times r_1^2}}$$

$$\text{or} \quad r_1 = \frac{4\pi^2 \times 4 \times m_e \times r_1^2 \times KZe^2}{n^2 h^2}$$

$$\text{or} \quad r_1 = \frac{n^2 h^2}{4 \times 4\pi^2 \times m_e \times KZe^2} = \frac{r}{4}$$

$$\text{or} \quad \frac{r_1}{r} = \frac{1}{4}$$

28. (a) $v_1 = \dfrac{nh}{2\pi m r_1} = \dfrac{nh}{2\pi \times 2m_e \times \dfrac{n^2 h^2}{16\pi^2 \times m_e \times KZe^2}}$

$$\text{or} \quad v_1 = \frac{4\pi \times KZe^2}{nh} = 2 \times \frac{2\pi \times KZe^2}{nh} = 2v$$

$$\text{or} \quad \frac{v_1}{v} = 2$$

29. (c) $\text{TE} = -\dfrac{1}{2}\,\text{KE} = E_1 = -\dfrac{1}{2} m_1 v_1^2$

$$\text{or} \quad E_1 = -\frac{1}{2} \times 2m_e \times \frac{16\pi^2 \times K^2 Z^2 \times e^4}{n^2 h^2}$$

$$\text{or} \quad E_1 = -8 \times \frac{2\pi^2\, K^2 \times Z^2 \times e^4 \times m_e}{n^2 h^2}$$

$$\text{or} \quad E_1 = 8 \times E$$

$$\text{or} \quad \frac{E_1}{E} = 8$$

DPP 3.3

Subjective Type

1. From the de Broglie relationship

$$\lambda = \frac{h}{mv}$$

$$\text{For CH}_4,\ \lambda_{CH_4} = \frac{h}{m_{CH_4} \times v_{CH_4}} \qquad \text{(i)}$$

$$\text{For O}_2,\ \lambda_{O_2} = \frac{h}{m_{O_2} \times v_{O_2}} \qquad \text{(ii)}$$

Wavelength of CH_4 and O_2 is equal, hence

$$\frac{h}{m_{CH_4} \times v_{CH_4}} = \frac{h}{m_{O_2} \times v_{O_2}}$$

$$\Rightarrow \quad \frac{v_{CH_4}}{v_{O_2}} = \frac{m_{O_2}}{m_{CH_4}} = \frac{32}{16} = 2$$

$$\therefore \quad v_{CH_4} = 2v_{O_2}$$

The velocity of CH_4 molecule is two times the velocity of O_2 molecule.

2. Mass of the ball = 40 g = 40×10^{-3} kg
The uncertainty in the speed

$$\Delta v = 45 \times \frac{2}{100} = 0.9 \text{ m s}^{-1}$$

So the uncertainty in position

$$\Delta x = \frac{h}{4\pi\, \Delta p} = \frac{h}{4\pi m\, \Delta v}$$

$$= \frac{6.626 \times 10^{-34}\text{ Js}}{(4 \times 3.14) \times (40 \times 10^{-3}\text{kg}) \times (0.9\text{ ms}^{-1})}$$

$$= 1.46 \times 10^{-33}\text{m}$$

3. Given that the uncertainty in position (Δx) is equal to de Broglie wavelength (λ), i.e., $\Delta x = \lambda$.
But according to de Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

$$\text{or} \quad \Delta x = \frac{h}{p} \qquad \text{(Given condition)}$$

According to Heisenberg uncertainty principle,

$$(\Delta x)(\Delta p) \geq \frac{h}{4\pi}$$

$$\left(\frac{h}{P}\right)\Delta p \geq \frac{h}{4\pi}$$

$$\frac{\Delta \cancel{p}}{\cancel{p}} \geq \frac{\cancel{h}}{4\pi \times \cancel{h}}$$

$$\frac{\Delta \cancel{p}}{\cancel{p}} \geq \frac{1}{4\pi} \text{ (Constant)}$$

4. $\lambda_1 = \dfrac{h}{\sqrt{2mq(100)}} = \dfrac{k}{10}$,

$\lambda_2 = \dfrac{h}{\sqrt{2mq(81)}} = \dfrac{k}{9}$

$\lambda_3 = \dfrac{h}{\sqrt{2mq(49)}} = \dfrac{k}{7}$

$$\frac{\lambda_3 - \lambda_2}{\lambda_1} = \left(\frac{\frac{k}{7} - \frac{k}{9}}{\frac{k}{10}}\right) = \frac{20}{63}$$

5. K.E. of ejected $e^- = E_P - \text{IE}_H$

$= 19.6 - 13.6 = 6$ eV

$\Rightarrow \quad \lambda = \dfrac{12.25}{\sqrt{E}} \text{ Å} = \dfrac{12.25}{\sqrt{6}} \text{ Å} = 5 \text{ Å}$

$= 7$

6. $\lambda = \dfrac{h}{\sqrt{2 \times m \times \text{K.E.}}}$

$$\lambda = \frac{6.6 \times 10^{-34}\,\text{Js}}{\sqrt{2 \times 9.1 \times 10^{-31}\,\text{kg} \times 5 \times 10^{-25}\,\text{J}}}$$

$= 6.94 \times 10^{-7}$ m

Single Correct Answer Type

7. (d) $\lambda = \dfrac{h}{\sqrt{2Em}}$

$$\frac{\lambda_m}{\lambda_{2m}} = \frac{h/\sqrt{2Em}}{h/\sqrt{2E(2m)}} = \frac{\sqrt{2}}{1}$$

8. (c) $\lambda = \dfrac{h}{\sqrt{mkT}}$

$$\frac{\lambda_1}{\lambda_2} = \sqrt{\frac{T_2}{T_1}} = \sqrt{\frac{1200}{300}} = 2$$

$\lambda_1 = 2\lambda_2 = 2\lambda$

9. (b) $\lambda_e = \dfrac{h}{m_e v_e}$

$\lambda_n = \dfrac{h}{m_n v_n}$

$\dfrac{h}{m_e v_e} = \dfrac{h}{m_n v_n}$

$v_n = \dfrac{m_e v_e}{m_n} = \dfrac{1}{1840} \times V_c \qquad \left(m_e = \dfrac{1}{1840} m_n\right)$

10. (b) de Broglie wavelength $(\lambda) = \dfrac{h}{p}$

or Δx (uncertainty in position) $= \dfrac{h}{p}$

$\therefore \quad \Delta x\, \Delta p = \dfrac{h}{4\pi}$

or $\quad \dfrac{h}{p} \times \Delta p = \dfrac{h}{4\pi}$

$\dfrac{\Delta p}{p} = \dfrac{1}{4\pi}$

or $\quad \dfrac{m \times \Delta v}{m \times v} = \dfrac{1}{4\pi}$

or $\quad \dfrac{\Delta v}{v} = \dfrac{1}{4\pi}$

$\therefore$ % (uncertainty in velocity) $= \dfrac{\Delta v}{v} = \dfrac{1}{4\pi} \times 100 \approx 8\%$

11. (b) $\lambda \propto \dfrac{1}{\sqrt{\text{KE}}} = \sqrt{\dfrac{\text{KE}_1}{\text{KE}_2}} = \dfrac{\lambda_1}{\lambda_2}$ or $\dfrac{\lambda_1}{0.99\lambda_1}$

$\Rightarrow \quad \text{KE}_2 = (0.99)^2\, \text{KE}_1 \approx 1.02\, \text{KE}_1$

% change in KE $= \dfrac{\text{KE}_2 - \text{KE}_1}{\text{KE}_1} \times 100 \approx 2\%$

12. (a) Heisenberg's uncertainty principle is

$\Delta x \geq \dfrac{h}{2\pi}$ $\qquad$ Given $\Delta x = \Delta p = m\Delta v$

$\Rightarrow \quad \Delta p \geq \sqrt{\dfrac{h}{4\pi}}$ i.e. $m\,\Delta v \geq \sqrt{\dfrac{h}{4\pi}}$

$\Rightarrow \quad \Delta v \geq \dfrac{1}{m}\sqrt{\dfrac{h}{4\pi}} \geq 8 \times 10^{12}\ \text{m s}^{-1}$

13. (d) $\lambda = \dfrac{h}{mv}$ distance travelled in one second by velocity V

$= \text{v cm} = \lambda$

$\lambda = \dfrac{h}{mv} \Rightarrow \lambda^2 = \dfrac{h}{m} \Rightarrow \lambda = \sqrt{\dfrac{h}{m}}$

14. (b) $r_1 = 0.529$ Å

$r_3 = 0.529 \times (3)^2$ Å $= 9x$

So, $\quad \lambda = \dfrac{2\pi r}{n} = \dfrac{2\pi(9x)}{3} = 6\pi x$

15. (b) Total energy $= \dfrac{13.6Z^2}{n^2} = \dfrac{13.6(Z)^2}{(4)^2} = 3.4$ eV

Now K.E. $= 3.4 - 1.4 = 2$ eV

Now, Total energy $= 2 + 4 = 6$ eV $\qquad$ i. e., potential $= 6$ V

For electron $\lambda = \sqrt{\dfrac{150}{V}}$, so $\lambda = 5$ Å.

Multiple Correct Answers Type

16. (b, d)

$\lambda = \dfrac{h}{m\upsilon}$

For same speed, $\lambda_A < \lambda_B$ because $m_A > m_B$.

17. (b, c)

Heisenberg principle is only for microscopic particles which are moving with a very high speed.

18. (a, b)

19. (a, b, d)

Heisenberg principle is $\Delta p.\Delta x = \frac{h}{2\pi} = \frac{\hbar}{2\pi} = \frac{\hbar}{2}$

$$m.\Delta u.\Delta x = \frac{h}{4\pi}$$

Note that the principle loses its significance if Δu and Δx are not considered along same axis.

20. (a, b)

According to de Broglie, an electron is having both particle as well as wave characteristics.

21. (a, b, c)

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mKE}} = \frac{h}{\sqrt{2mqV}}$$

Where v, KE and V are same, as m increases λ decreases. $\lambda_e > \lambda_p > \lambda_\alpha$ (if v, KE and V are same).

Matching Column Type

22. (a → r), (b → p), (c → q, s), (d → r)

Integer Type

23. (8) Given $\Delta x = \lambda$

$$\Delta x.\Delta p \geq \frac{h}{4\pi} \text{ as } \lambda = \frac{h}{mv} \Rightarrow h = \lambda \text{ mv}$$

$$\lambda \times m\, \Delta v \geq \frac{\lambda mv}{4\pi}$$

$$\Rightarrow \frac{\Delta v}{v} \geq \frac{1}{4\pi}$$

$$\Rightarrow \frac{\Delta v}{v}\% \geq \frac{1}{4\pi} \times 100 = 7.9 \approx 8$$

24. (4) $m = -l \ldots\ldots 0 \ldots\ldots +l$

If m has maximum value 3, then $l = 3$.

$l = 0 \ldots\ldots n - 1 \Rightarrow n = 4$

No. of deBroglie waves is equal to value of n.

Comprehension Type

25. (a) $\Delta x\, .\, \Delta p \geq \frac{h}{4\pi} \Rightarrow \Delta p \geq \sqrt{\frac{h}{4\pi}}$ [∵ $\Delta x = \Delta p$ (given)]

$$\Rightarrow \Delta v \geq \frac{1}{m}\sqrt{\frac{h}{4\pi}} = 8 \times 10^{12} \text{ ms}^{-1} \ [\because \Delta p = m\,\Delta v]$$

26. (b) $\Delta v = 2 \text{ cm s}^{-1} = 2 \times 10^{-2} \text{ m s}^{-1}$

$$\Delta x\, .\, m\,\Delta v \geq \frac{h}{4\pi} \Rightarrow \Delta x \geq \frac{h}{4\pi} \times \frac{h}{m\Delta v}$$

$$\Delta x = \frac{6.626 \times 10^{-34}}{4\pi \times 10^{-3} \times 2 \times 10^{-2}} = 2.64 \times 10^{-30} \text{ m}$$

DPP 3.4

Subjective Type

1. At nodal point, $\psi = 0$. From the given wave function, we find that $\psi = 0$ at following values of r:

$$\left[27 - 18\left(\frac{r}{a_0}\right) + 2\left(\frac{r}{a_0}\right)^3\right] = 0$$

Solving for r_0/a_0, we get

$$\frac{r_0}{a_0} = \frac{18 \pm \sqrt{18^2 - 216}}{4} = \frac{18 \pm 10.4}{2}$$

Hence $r = 14.2a_0$ and $r_0 = 3.9a_0$

Besides there is a node at $r = \infty$.

2. $\mu = \sqrt{n(n+2)} = \sqrt{35} \Rightarrow n^2 + 2n = 35 \Rightarrow n^2 + 2n - 35 = 0$, Taking +ve value

So, $n = 5$

$X^{3+} = 5 + 3 = 8$

$= 3d^6 3s^2$

So, Fe = 26.

3. (a) Total number of electrons = (2 + 8 + 6) = 16

So, Atomic number = 16

Electronic configuration = $1s^2$, $2s^2 2p^6$, $3s^2 3p^4$

(b) Total number of s-electrons = $(1s^2 + 2s^2 + 3s^2) = 6$

(c) Total number of p-electrons = $(2p^6 + 3p^4) = 10$

(d) Total number of d-electrons = 0

4. $n = 3, l = 0, m = 0$ $\quad m_s = -\frac{1}{2}, 0, +\frac{1}{2}$

$$l = 1;\ m = -1, 0, +1 \left\langle \begin{array}{l} m_s = -\frac{1}{2}, 0, +\frac{1}{2} \\ m_s = -\frac{1}{2}, 0, +\frac{1}{2} \\ m_s = -\frac{1}{2}, 0, +\frac{1}{2} \end{array} \right.$$

$l = 2;\ m = -2, -1, 0, +1, +2$ $\quad \left\{ m_s = -\frac{1}{2}, 0, +\frac{1}{2} \text{ for each value of magnetic quantum no.} \right\}$

Number of elements = $3s(3e)$

$3p(9e)$

$3d(15e)$

∴ 27 elements will be there in third period of periodic table.

5. (a) $\mu_l = \sqrt{l(l+1)}\frac{h}{2\pi}$ for $3p$, $l = 1 \Rightarrow \mu_l = \sqrt{2}\,\hbar$

(b) $\mu_l = \sqrt{6}\hbar$ for $3d$, $l = 2$

(c) $\mu_l = 0$ for $3s$, $l = 0$

6. Number of angular node = $l = 2$

$l = 2$

Number of radial node = $n - l - 1$

$\Rightarrow 2 = n - l - 1$

$\Rightarrow n = 5$

So, $(n + l) = 7$.

Single Correct Answer Type

7. (a) For $m_l = +2$ (maximum), $l = 2$ and $n = 3$

Number of waves in a shell $= n = 3$

8. (c) Option (c) represents the distribution of $l = 2$ for H atom,

(a) Two nodes: $(n - l - 1) = 2$, $(n - 2 - 1) = 2$

$\therefore n = 5$ (High value of n)

(b) One node: $(n - 2 - 1) = 1$, $n = 4$.

(c) Zero node: $(n - 2 - 1) = 0$, $n = 3$. (Minimum value of n for which $l = 2$ is allowed)

(d) Graph does not correspond to any radial distribution curve.

9. (d) $n \neq m$

10. (c) As an orbital can have maximum of two electrons with opposite spin.

11. (b) In X: $l = d$

In Y, $l = s$

Energy of $d > s$.

12. (b) $5f^{14}$, $6d^3 \Rightarrow 17e^-$

$5f^{14} = (n + l) = 5 + 3 = 8$

$6d^3 = (n + l) = 6 + 2 = 8$

13. (b) Option (b) is correct plot because only for 2*s*-orbital, there will be single node.

Number of node $= n - l - 1$

$= 2 - 0 - 1 = 1$

14. (c)

15. (c) The lobes of $d_{x^2-y^2}$ orbital are aligned along X and Y axis. Therefore the probability of finding the electron is maximum along x and y axis.

Multiple Correct Answers Type

16. (b, c, d)

Option (a) is not possible because an orbital can be defined only by the three quantum numbers '*n*', '*l*' and '*m*'.

17. (a, b, d)

18. (b, c)

$$\left.\begin{aligned} Fe^{3+} &= 26 - 3 = 23 \\ Mn^{+} &= 25 - 1 = 24 \\ Cr &= 27 = 27 \end{aligned}\right\}$$

$Cu^+ \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3p^{10}$

No unpaired e^-, so it is not coloured salt.

19. (a, c)

In option (A) is not considered Hund's rule and in option (C), Mn has 3 unpaired electrons, so $\sqrt{3}$ BM.

20. (a, c)

$3d$, $4s$

b is wrong as n and l cannot be the same.

d is wrong as m cannot be greater than l.

21. (a, b, c)

$n = 4$, $m = 2$

Value of $l = 0$ to $(n - 1)$ but $m = 2$.

Value of s may be $+1/2$ or $-1/2$.

Matching Column Type

22. (a → p), (b → q), (c → r), (d → s), (e → t)

23. (A → Q), (B → P), (C → S), (D → R)

Spin multiplicity $= 2N + 1 = S$

$N =$ total spin $= \frac{n}{2}$ where $n =$ no. of unpaired e^-s of same spin

For (A), $n = 2$, $N = 1$, $S = 3$ (A) → (Q)

For (B), $n = 0$, $N = 0$; $S = 1$(B) → (P)

For (C) $n = 0$, $N = 0$, $S = 1$ (C) → (S)

(D) → (R) ; since no. of unpaired electrons of same spin is the highest. Therefore in this excited state of C, maximum exchanges of e^- between same spin will occur.

Integer Type

24. (b) $Fe^{2+} = [Ar]\,3d^6$ $\quad n = 4,\ \mu = \sqrt{n(n+2)}$ BM

$Mn^{2+} = [Ar]\,3d^5$ $\quad n = 5,\ \mu = \sqrt{24}$ BM

$Cr^{2+} = [Ar]3d^4$ $\quad n = 4,\ \mu = \sqrt{35}$ BM

$Ni^{2+} = [Ar]3d^8$ $\quad n = \mu = \sqrt{8}$ BM

$n =$ no. of unpaired electrons.

25. (4) Spin multiplicity

$$= 2S + 1 = 2 \times \frac{3}{2} + 1 = 4\left(S = s_1 + s_2 + s_3 = \frac{1}{2} + \frac{1}{2} + \frac{1}{2}\right)$$

26. (7)

(The next electron will enter into $5d$ subshell whose $(n + l)$ will be equal to 7 (seven).

Comprehension Type

27. (b) $m_s = +\frac{1}{2}$ for clockwise spin

$m_s = -\frac{1}{2}$ for anticlockwise spin

$\therefore$ components of spin angular momentum vector around the chosen axis are limited to $\pm\frac{1}{2}\frac{h}{2\pi}$.

28. (a) number of unpaired electrons in Fe^{3+} are 5.

$\therefore$ Total spin $= 5 \times \frac{1}{2}$

29. (c) Magnetic quantum number specifies orientations of orbitals in space.

30. (b) The energy of an electron in an atomic orbital of a multi-electron atom depends on the principal and azimuthal quantum number only.

CHAPTER 4

DPP 4.1

Subjective Type

1. Maximum capacity or volume of balloon $= \frac{8}{7} \times 480 = 548.57$ mL

Also, $V_1 = 480$ mL, $T_1 = 278$ K, $n = 1$ mole

(a) The balloon will burst at the temperature say T_2 when volume becomes 548.57 mL.

$$\because \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{480}{278} = \frac{548.57}{T_2}$$

$\therefore T_2 = 317.71, K = 44.71°C$

Thus, balloon will not burst at 30°C.

(b) The minimum temperature at which balloon burst is 44.71°C.

2. Given, $V = 10$ litre $\quad P = 3$ atm $\quad T = 290$ K

(a) After driving $V = 10$ litre $\quad P = ?$ $\quad T = 320$ K

$\because \frac{P_1}{P_2} = \frac{T_1}{T_2}$, (at constant V of tyre)

$$\frac{3}{P} = \frac{290}{320}$$

$\therefore P = 3.31$ atm.

(b) At 47°C

Now volume is to be taken out so that tyre is left at a pressure of 3 atm, i.e., decrease in pressure as a result of it.

$= 3.31 - 3.0 = 0.31$ atm

At 0.31 atm, volume of air is 10 litre and therefore, at 1 atm this air will occupy V litre.

$\because P_1V_1 = P_2V_2$ (temperature is 47°C)

$\therefore 0.31 \times 10 = 1 \times V_2$

$\therefore V_2 = 3.1$ litre.

3. Pressure at 100 meter depth = Atmospheric pressure + Pressure of water

$= 76 \times 13.6 \times 981 + 100 \times 100 \times 1 \times 981$

$= 1013961.6 + 9810000 = 10823961.6$ dyne cm^{-2}

Let volume of balloon at the surface level be V_i cm^3 and the volume of balloon at the depth of 100 meter is V_f, then

$P_1V_1 = P_2V_2$

$\therefore 76 \times 13.6 \times 981 \times V_i = 10823961.6 \times V_f$

$$\therefore V_f = \frac{76 \times 13.6 \times 981}{10823961.6} \times V_i$$

$V_f = 0.0937\ V_i$

$\therefore \quad V_f = 9.37\%$ of V_i.

4. Given, $P_1 = 250$ kPa, $T_1 = 300$ K

$P_2 = 1 \times 10^6$ Pa, $T_2 = ?$

Since, volume of cylinder remains constant.

Therefore, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{250 \times 10^3}{300} = \frac{1 \times 10^6}{T_2}$$

$\therefore \quad T_2 = 1200$ K.

Single Correct Answer Type

5. (c) $P_1V_1 = P_2V_2$

or $\frac{P_1}{P_2} = \frac{V_2}{V_1}$

$$\frac{10}{7} = \frac{1000 - V_{\text{doll}}}{800 - V_{\text{doll}}}$$

$8000 - 10\ V_{\text{doll}} = 7000 - 7\ V_{\text{doll}}$

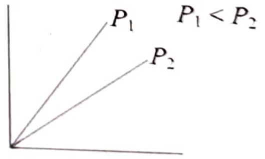
$3\ V_{\text{doll}} = 1000$

$V_{\text{doll}} = \frac{1000}{3}$ mL

6. (b) $V_t = V_0 \left(\frac{273 + t}{273}\right)$

or $\frac{V}{T}$ = constant (P & mass constant)

So,



Higher the pressure, less is the slope of line.

7. (a) Suppose volume of 200 mg of air at 17°C = V mL

As pressure remains constant (being an open vessel), applying Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}, \text{ i.e., } \frac{V}{290} = \frac{V_2}{390} \text{ or } V_2 = 1.34\ V$$

$\therefore$ Volume of air expelled $= 1.13\ V - V = 0.34\ V$

Mass of 1.34 V air at 117°C = 200 mg

Mass of 0.34 V air at 117°C $= \frac{200}{1.34} \times 0.34$ mg

$\therefore$ Mass % of air expelled $= \frac{200 \times 0.34}{1.34} \times \frac{1}{200} \times 100 = 25.37\%$

8. (b) Difference of mercury levels in the two arms $= 43.7 - 15.6$
$= 28.1$ cm

As level in the limb connected to the gas bulb is lower than that of the open limb, this means pressure of gas is more than the atmospheric pressure.

∴ Pressure of the gas in the bulb = Barometric pressure + Difference of mercury levels

= 74.3 cm + 28.1 cm = 102.4 cm

$$= \frac{102.4}{76} \text{atm} = \frac{102.4}{76} \times 1.01325 \text{ bar} = 1.365 \text{ bar}$$

9. (c) $V_2 = \left(\frac{V_1}{T_1}\right) T_2 = \left(\frac{22.4 \text{ L}}{273 \text{ K}}\right)(373 \text{ K}) = 30.6 \text{ L}$

10. (b) At constant temperature T, $V \propto \frac{1}{P}$ (for 1 mol gas).

Thus, correct sequence of volume will be:

$V_1 > V_2 > V_3 > V_4$

11. (b) Let $\frac{1}{P^2} = Y$

$\therefore \ P = \frac{1}{\sqrt{Y}}$

if $X = V = \frac{K}{P} = K\sqrt{Y}$

or $X^2 = K^1 \ Y$ i.e., curve (b).

Multiple Correct Answers Type

12. (a, b, c)

(a) $V_t = V_0 + \frac{t/°\text{C}}{273} V_0$; intercept is not zero

(b) $V_T = KT$; intercept is zero

(c) $V = KT$; slope is K

13. (a, c)

Boyle's law $P \propto \frac{1}{V}$

$\therefore \quad \left(\frac{\partial P}{\partial V}\right)_V = -K/V^2$

14. (a, b, c, d)

(a) $P \propto \frac{1}{V}$ Boyle's law

(b, c) $P \propto T$

$P = kT$

$\log P = \log T + \log k$

(d) $P = \frac{k}{V} \Rightarrow \log P = \log k + \log \frac{1}{V}$

$\log P = \log k - \log V$

$\log P = -1 \times \log V + \log k$

$y = mx + C$

15. (b, c, d)

According to Charles' law: $V \propto T$, so, V vs T graph will be a straight line.

According to Boyle's law: $V \propto \frac{1}{P}$, so, we will get a graph given in options (b) and (d) .

16. (d)

$P = \frac{C}{V}$ where C is a constant. We can see that (c) is true as the graph of P vs $\frac{1}{V}$ would be a straight line.

(a) is true because $\log P = \log C - \log V$.

(b) is true because $\frac{dP}{dV} = \frac{-C}{V^2}$

which means that as V increases the slope decreases and is always negative.

Matching Column Type

17. (a → q; b → p; c → r)

For Boyle's law: PV is constant

For Charles' law: $V \propto T$

For Gay-Lussac's law: $P \propto T$.

Integer Type

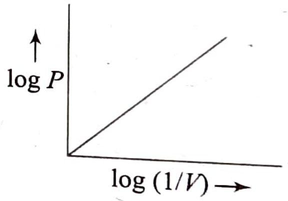
18. (1)

Here, $P_1 = 1$ bar, $P_2 = 3.1$ bar, $V_1 = 3.15$ L, $V_2 = ?$

From Boyle's law equation $P_1V_1 = P_2V_2$, we get

$$V_2 = \frac{P_1V_1}{P_2} = \frac{1.00 \text{ bar} \times 3.15 \text{ L}}{3.1 \text{ bar}} = 1.01 \text{ L}$$

19. (1) According to Boyle's law, $P = \frac{K}{V}$. Taking log both sides, we get



$\log P = \log (1/V) + \log K$

Comparing it to $y = mx + C$, we get

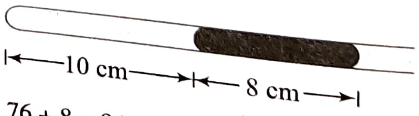
where C is intercept along y-axis = $\log K$

$K = 10.23$

$\therefore \log (10.23) = 1.009 \approx 1$

Comprehension Type

20. (b) $P_1V_1 = P_2V_2$ or $P_1 l_1 a = P_2 l_2 a$



$\because P_2 = 76 + 8 = 84$ cm

$\therefore \ l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{84} = 9.05$ cm

21. (c) $P_1 l_1 a = P_2 l_2 a$

$\because \quad P_2 = 76 - 8 = 68$ cm

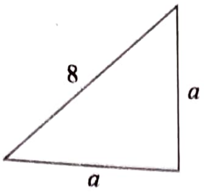
$\therefore \quad l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{68} = 11.18$ cm

22. (a) When the tube is held at 45° with open end up, the mass of Hg is borne partially by the gas and partially by the Hg. Vertical height of Hg a measure of additional pressure on gas, i.e.,

$$l = \frac{8}{\sqrt{2}}$$

Also $P_2 l_2 a = P_1 l_1 a$

$$l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{76 + \frac{8}{\sqrt{2}}} = 9.3 \text{ cm}$$



DPP 4.2

Subjective Type

1. Given $P_1 = P$, $V_1 = V$, $T_1 = T$

$P_2 = P_2$, $V_2 = V - \frac{5\text{ V}}{100}$, $T_2 = T$

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ or } P \times V = P_2 \times \left(V - \frac{5\text{ V}}{100}\right)$$

or $P_2 = \frac{100}{95} P$

$\therefore$ Increase in $P = 0.0526$

$\therefore$ % increase in $P = 0.0526 \times 100 = 5.26$.

2. **Case I:** Given,

$P = 1$ atm, $w = 1$ atm $T = (t + 273)$ K, $V = V$ litre

Case II:

$T = (t + 283)$; $P = 1 + \frac{10}{100}$ $w = 12$ g $V = V$ litre

$= 1.1$ atm

Using gas equation:

Case I: $1 \times V = \frac{12}{M} \times R(t + 273)$

Case II: $1.1 \times V = \frac{12}{M} \times R(t + 283)$

By Eqs. (1) and (2), $\frac{1.1}{1} = \frac{t + 283}{t + 273}$

$\therefore 1.1t + 300.3 = t + 283$

$\therefore 0.1t = -173°\text{C} = 100 \text{ K}$

Also, from Case I $1 \times V = \frac{12}{120} \times 0.082 \times 100$ $(\because M = 120)$

$V = 0.82$ litre.

3. For B – H compound,

$P = 0.658$ atm, $V = \frac{407}{1000}$ litre, $T = 373$ K, $w = 0.553$ g

$$\therefore PV = \frac{w}{M} RT$$

$$0.658 \times \frac{407}{1000} = \frac{0.553}{\text{M}} \times 0.0821 \times 373$$

$M = 63.23 \text{ g mol}^{-1}$

$\because$ 100 g compound has 85.7 g B.

$\therefore$ 63.23 g compound has $= \frac{85.7 \times 63.23}{100}$ g B $= 54.19$ g B

$\frac{54.19}{10.8}$ g – atom of $B = 5$ g – atom of B

$\therefore$ Formula becomes B_5H_x.

$\therefore$ $5 \times 10.8 + x = 63.25$

$x = 9.25 = 9$ (an integer)

$\therefore$ Formula of compound is B_5H_9.

4. We know that $PV = nRT$

Volume occupied by 1 mol gaseous water at 100°C and 1 atm pressure

$$= \frac{1 \times 0.0821 \times 373}{1} = 30.62 \text{ litre}$$

Volume of 1 mol liquid water $= \frac{\text{mass}}{\text{density}} = \frac{18}{0.958}$

$= 1.88 \times 10^{-2}$ litre

% of volume occupied by liquid water

$$= \frac{1.88 \times 10^{-2}}{30.62} \times 100 = 0.0613\%$$

% of free volume $= 100 - 0.0613 = 99.93\%$

Single Correct Answer Type

5. (c) Let x be the mole fraction of NH_3 in the original mixture.

Atomic of gas to start with = 1 mol

Atomic of gas at the end $= 2x$ mol $+ 3(1 - x)$ mol $= (3 - x)$ mol

Since, $pV = nRT$, we have

$$\frac{n_1T_1}{n_2T_2} = \frac{p_1}{p_2} \Rightarrow \left(\frac{1}{3 - x}\right)\left(\frac{300}{1000}\right) = \frac{0.6}{4.8} = \frac{1}{8}$$

Hence $x = 0.6$.

Mole per cent of $NH_3 = 60\%$

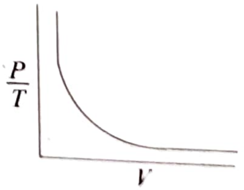
6. (b) $P = \frac{d}{M} RT$

$$\therefore \frac{d}{p} \propto \frac{1}{T} \text{ or } \frac{d_1}{p_1} \times \frac{p_2}{d_2} = \frac{1}{283} \times \frac{383}{1}$$

$$\therefore \frac{d_2}{p^2} = \frac{d_1}{p_1} \times \frac{283}{383}$$

$$\therefore \frac{d_2}{P_2} = \frac{283 \cdot X}{383} = \frac{283X}{383}$$

7. (d) Option (a) represents Charles' law, option (b) represents Boyle's law, option (c) represents $P - T$ law, option (d) does not obey ideal gas laws as $PV = nRT$ or $\frac{P}{T} = \frac{K}{V}$. An increase in V will decrease in $\frac{P}{V}$ like



8. (a) log $V \propto$ log T at constant pressure

$$PV = nRT$$

$$0.821 \text{ V} = 10 \times 0.082 \times T$$

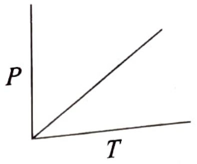
$$\frac{V}{T} = \text{Constant} = 1$$

Slope of the line will be 1, i.e., angle will be 45°.

9. (a) $\frac{PV}{T}$ = constant $\Rightarrow \frac{PV}{T_1} = \frac{3P \cdot 3V}{T_2}$

$T_2 = 9T_1$

Temperature increased to nine times of its initial value.



Multiple Correct Answers Type

10. (a, b, c)

The equations of an ideal gas are

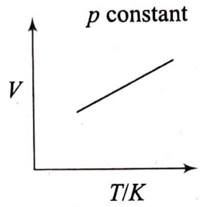
$pV = nRT$

$pV = nRT = (m/M)RT; p = (m/M)RT/M = \rho RT/M$

$pV = (1/3)\text{mN}\overline{u^2}$

11. (a, c, d)

The abbreviation STP stands for standard temperature and pressure where temperature is 0°C and pressure is 1 atm.



$\frac{\rho}{P} = \frac{M}{RT}$

12. (a, b)

Comparing with $PV = nRT$.

13. (b, c)

(b) From $PV = \frac{w}{M} RT$

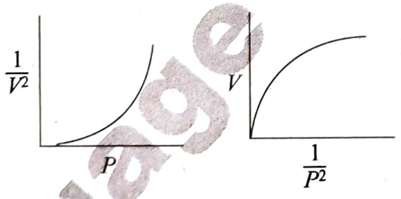
$T \propto \frac{1}{P}$ (at const. V and w)

(c) $T \propto \frac{1}{w}$ (at const. V and P)

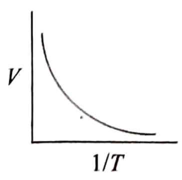
Matching Column Type

14. (a → r), (b → s), (c → p), (d → q)

- From $PV = nRT$ at constant T and n
  PV = constant
  So, plot of $1/V^2$ vs P and plot of V vs $1/P^2$ can be shown as



- Plot of V vs $1/T$ at constant P and n verifies Charles law and can be represented as:



- Plot of P vs T at constant V and n verifies Gay-Lussac's law and can be represented as

Integer Type

15. (2) $x = 2 \times 0.0821 \times \frac{540}{44.8} = 1.97 \approx 2.$

16. (2) $PV = nRT, R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}.$

Comprehension Type

17. (d) $n_{H_2} = \frac{PV}{RT} = \frac{20000}{RT}$

$n_{He} = \frac{PV}{RT} = \frac{20000}{RT}$

$\therefore \quad n_{H_2} + n_{He} = \frac{40000}{RT}$

Total volume = 300 mL

$p = \frac{n}{V} RT = \frac{40000\,RT}{RT \times 300} = \frac{400}{3} = 133.33$ Torr

18. (a) $p(O_2) = 787 - 27 = 760$ Torr = 1 atm

$p = \frac{n}{V} RT$

$\therefore \quad 1 = \frac{n}{3} \times 0.0821 \times 300, n = 0.122$ mol

19. (a) $C_3H_8 = n_1$ mol

$CH_4 = n_2$ mol

Total mol = $(n_1 + n_2)$

$\therefore$ Mole fraction of $C_3H_8 = \left(\frac{n_1}{n_1 + n_2}\right)$

$p = \frac{n}{V} RT$

$320 = \frac{(n_1 + n_2)}{V} RT$

$\underset{n_1}{C_3H_8} \xrightarrow{\text{air oxidation}} RT$

$\underset{n_2}{CH_4} \xrightarrow{\text{air oxidation}} \underset{n_2}{CO_2}$

$\therefore \quad 448 = \frac{(3n_1 + n_2)RT}{V}$

$\therefore \quad \frac{448}{320} = \frac{3n_1 + n_2}{n_1 + n_2}$

$1.4(n_1 + n_2) = 3n_1 + n_2$

$n_2 = 0.25\, n_2$

$\therefore$ Mole fraction of $C_3H_8 = \frac{0.25\, n_2}{0.25\, n_2 + n_2} = 0.2$

20. (d) $p = \frac{nRT}{V} = \frac{w}{mV}RT = \frac{dRT}{m}$

Let N_2 be $= w_1$ g with x %.

O_2 be $= w_2$ g with $(100 - x)$%

$\therefore\ \overline{M} = \frac{m_1 x + m_2(100 - x)}{x + (100 - x)}$

$31.2 = \frac{28x + 32(100 - x)}{100}$

$\therefore x = 20$

$\therefore\ N_2 = 20\text{ g} = \frac{20}{28}\text{ mol} = 0.71\text{ mol}$

Thus, $O_2 = 80 = \frac{80}{32}\text{ mol} = 2.50\text{ mol}$

$\therefore$ Mole fraction of $N_2 = \frac{0.71}{3.21} = 0.22$

DPP 4.3

Subjective Type

1. Given, $V = 10$ litre, $T = 27 + 273 = 300$ K

Mole of He $= \frac{0.4}{4} = 0.10$

Mole of $O_2 = \frac{1.6}{32} = 0.05$

Mole of $N_2 = \frac{1.4}{28} = 0.05$

$\therefore$ Total mole $= 0.10 + 0.05 + 0.05 = 0.20$

$$P_M = \frac{nRT}{V} = \frac{0.20 \times 0.082 \times 300}{10} = 0.492\text{ atm}$$

$$P'_{He} = P_M \times \text{mole fraction of He} = 0.492 \times \frac{0.10}{0.20} = 0.246\text{ atm}$$

$$P'_{O_2} = P_M \times \text{mole fraction of } O_2 = 0.492 \times \frac{0.05}{0.20} = 0.123\text{ atm}$$

$$P'_{N_2} = P_M \times \text{mole fraction of } N_2 = 0.492 \times \frac{0.20}{0.20} = 0.123\text{ atm}$$

2. Given, mass of CH_4 = mass of $O_2 = wg$, $V = 1$ litre, $T = 300$ K

(a) Mole fraction of $CH_4 = \frac{w/16}{w/16 + w/32} = \frac{2}{3}$

Mole fraction of $O_2 = \frac{w/32}{w/16 + w/32} = \frac{1}{3}$

$\because\ P'_{O_2} = P_M \times$ mole fraction of O_2
(Dalton's law of partial pressure)

$\therefore\ \frac{P'_{O_2}}{P_M} =$ mole fraction of $O_2 = \frac{1}{3}$

(b) $P'_{CH_4} \times 1 = (32/16) \times 0.0821 \times 300 = 49.26$ atm

$P'_{O_2} \times 1 = (32/32) \times 0.0821 \times 300 = 24.63$ atm

$\therefore\ O_M = P'_{CH_4} \times P'_{O_2} = 49.26 + 24.63 = 73.89$ atm

3. Given, mass of gas $A = 0.50$ g, molar mass of gas $A = 60$ mass of gas $B = 0.2$ g, molar mass of gas $B = 45$, $P_M = 750$ mm From Dalton's law of partial pressure

$$P'_A = P_M \times \text{mole fraction of } A = 750 \times \frac{0.5/60}{\left(\frac{0.5}{60}\right) + \left(\frac{0.2}{45}\right)} = 489.23\text{ mm}$$

Now, $P_M = P'_A + P'_B$

$\therefore\ P'_B = P_M + P'_A = 750 - 489.23 = 260.77$ mm

4. For gaseous mixture 80% O_2, 20% gas

$\therefore$ Average molar mass of mixture (M_m)

$$= \frac{32 \times 80 + 20 \times m}{100} \qquad (1)$$

Now for diffusion of gaseous mixture and pure O_2

$$\frac{r_{O_2}}{r_m} = \sqrt{\left(\frac{M_m}{M_{O_2}}\right)}$$

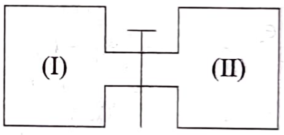
or $\frac{V_{O_2}}{t_{O_2}} \times \frac{t_m}{V_m} = \sqrt{\left(\frac{M_m}{M_{O_2}}\right)}$ ($\because$ same volume diffuses)

$$\therefore\ \frac{1}{224} \times \frac{234}{1} = \sqrt{\left(\frac{M_m}{32}\right)}$$

$$M_m = 34.92 \qquad (2)$$

By Eqs. (1) and (2), molar mass of gas $m = 46.6$.

5.



At STP

Before diffusion

$$\left.\begin{aligned} D_2 &= 1.12\text{ lit. at STP} = 0.2\text{ g} = 0.05\text{ mole} \\ H_2 &= 224\text{ lit. at STP} = 0.2\text{ g} = 0.1\text{ mole} \end{aligned}\right\}\text{ in bulb I}$$

When these moles are placed in the bulb, the partial pressure of gas will be different because V and T are constant. Also $P \propto n$.

Thus, $\frac{P_{D_2}}{P_{H_2}} = \frac{0.05}{0.10} = \frac{1}{2}$

After diffusion D_2 left in I bulb $= 0.1$ g

or D_2 diffuses from I into II (bulb) $= 0.2 - 0.1 = 0.1$

Now for diffusion D_2 and H_2

$$\frac{r_{D_2}}{r_{H_2}} = \sqrt{\left(\frac{M_{H_2}}{M_{D_2}}\right)} \times \frac{P_{D_2}}{P_{H_2}}$$

$$\because\ \frac{w_{D_2}}{t_{D_2}} \times \frac{t_{H_2}}{t_{H_2}} = \sqrt{\left(\frac{M_{D_2}}{M_{H_2}}\right)} \times \frac{P_{D_2}}{P_{H_2}}$$

$$\therefore\ \frac{0.1}{t} \times \frac{t}{w_{H_2}} = \sqrt{\left(\frac{4}{2}\right)} \times \frac{1}{2} \qquad \therefore w_{H_2} = 0.14\text{ g}$$

$\therefore$ Mass of gases in bulb II.

= mass of D_2 + mass of $H_2 = 0.10$ g $+ 0.14$ g $= 0.24$ g

$\therefore$ % D_2 by mass $= \frac{0.10}{0.24} \times 100 = 41.66\%$

% H_2 in bulb II $= 58.33\%$

Single Correct Answer Type

6. (d) We have $r_2 = \left(\frac{M_1}{M_2}\right)^{1/2} r_1 = \left(\frac{4}{64}\right)^{1/2} r_1 = \frac{r_1}{4}$

Since $r = n/t$, we get $r_2/r_1 = n_2/n_1$ i.e., $n_2 = (r_2/r_1)n_1$

$$n_2 = \left(\frac{1}{4}\right)\left(\frac{3\text{g}}{4\text{g}}\text{mol}^{-1}\right) = \frac{3}{16}\text{mol};$$

$$m_2 = \left(\frac{3}{16}\text{mol}\right)(64\text{ g mol}^{-1}) = 12\text{ g}$$

7. (b) $\frac{t_2}{t_1} = \left(\frac{M_2}{M_1}\right)^{1/2}$. For the choice a, $t_2/t_1 = \sqrt{2}$, for the choice b, $t_2/t_1 = 4$. For the choice e, $t_2/t_1 = \sqrt{14}$. For the choice d, $t_2/t_1 = \sqrt{22}$.

Thus, the choice (b) is correct.

8. (a) We have $\underset{n(1-\alpha)}{A_2(g)} = \underset{2n\alpha}{2A(g)}$

Total amount of gases $= n(1 - \alpha) + 2n\alpha = n(1 + \alpha)$

Average molar mass of gases

$$= \frac{n(1-\alpha)}{n(1+\alpha)}M_{A_2} + \frac{2n\alpha}{n(1+\alpha)}M_A = \frac{M_{A_2}}{1+\alpha}$$

According to Graham's law $\frac{r_{\text{mix}}}{r_X} = \left(\frac{M_X}{M_{\text{av}}}\right)^{1/2} = \left[\frac{M_X}{M_{A_2}/(1+\alpha)}\right]^{1/2}$

which gives $\alpha = \left(\frac{M_{A_2}}{M_X}\right)\left(\frac{r_{\text{mix}}}{r_X}\right)^2 - 1$

9. (c) $\because P' = P_T \cdot X_M$ and $V' = V_T \cdot X_M$

where X_M is mole fraction

Also $\frac{P'}{P_T}$ = Pressure fraction i.e., X_P

and $\frac{V'}{V_T}$ = Pressure fraction i.e., X_V

$\therefore X_M = X_P = X_V$

10. (c) From Dalton's partial pressure law

$$P_1 = \frac{1000}{1500} \times 600 + \frac{500}{1500} \times 800$$

$$= 400 + \frac{800}{3} = \frac{2000}{3} \text{ torr.}$$

$V_1 = 1500$ mL

$P_2 = ?$ $\quad V_2 = 2\text{ L} = 2000$ mL

From $P \propto \frac{1}{V}$

$$\frac{P_1}{P_2} = \frac{V_2}{V_1} \Rightarrow \frac{2000/3}{P_2} = \frac{2000}{1500}$$

$$\Rightarrow P_2 = \frac{1500}{3} = 500 \text{ torr.}$$

Multiple Correct Answers Type

11. (b, c)

These gas mixture react with each other.

12. (a, b, c)

According to Graham's law of diffusion:

$r_1 \propto \frac{1}{\sqrt{d_1}}$ and $r_2 \propto \frac{1}{\sqrt{d_2}}$ where d_1 and d_2 are densities of gases A and B.

Also, as molecular mass is twice the vapour density

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

and as $r \propto P$

$$\therefore \frac{r_1}{r_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}}$$

13. (a, c, d)

$$\text{Moles of } O_2 = \frac{W}{\text{Molar weight}} = \frac{20}{2} = 10 \text{ mol}$$

$$\text{Moles of } O_2 = \frac{W}{\text{Molar weight}} = \frac{128}{32} = 4 \text{ mol}$$

Total pressure

$$P = P_{H_2} + P_{O_2} = (n_{H_2} + n_{O_2})\frac{RT}{V}$$

$$= (10 + 4)\frac{(0.082 \times 473)}{20} = 27.15 \text{ atm}$$

1 atm = 760 mm = 1.013×10^6 dynes cm^{-2}.

$\therefore$ Total pressure = 20634 mm = 27.50×10^6 dynes cm^{-2}.

14. (a, c, d)

Rate of diffusion $\propto \sqrt{\frac{1}{M}}$

Hence, H_2 will diffuse into balloon and its size will increase.

Matching Column Type

15. (a → q), (b → s), (c → p, s), (d → p, q, r)

$$PV = nRT$$

When V and T are constant, then $P \propto n$.

(a → q)

(b) $d = \frac{PM}{RT}$ $\quad \therefore \frac{d_{\text{moist}}}{d_{\text{dry}}} = \frac{M_{\text{moist}}}{M_{\text{dry}}} < 1$

(b → s)

(c) $p^{\circ}_{H_2O} > p_{H_2O}$, hence $\frac{p_{H_2O}}{p^{\circ}_{H_2O}} < 1$ and $p^{\circ}_{H_2O}$ is also a function of temperature.

(c → p, s)

Dalton's law of partial pressure are applicable for only ideal gases.

(d → p, q, r)

Integer Type

16. (2)

Partial pressure $= \chi \times P_T$.

17. (2) $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{16}{4}} = 2$

Comprehension Type

18. (b) Gas A — Gas B

$W_A = 10$ g — $W_B = ?$

$M_A = 81$ — $M_B = 100$

$P_A = 10$ atm — $P_B = 20$ atm

$t_A = 1050$ particles — $t_B = 75$ min

$$\frac{W_A}{W_B} \times \frac{t_B}{t_A} = \frac{P_A}{P_B}\sqrt{\frac{M_A}{M_B}}$$

On putting all values,

$$\frac{10 \times 75}{W_B \times 50} = \frac{10}{20}\sqrt{\frac{81}{100}} = \frac{10 \times 9}{20 \times 10} = \frac{9}{20}$$

$$\frac{750}{W_A \times 50} = \frac{9}{20} W_B = \frac{750 \times 20}{50 \times 9} = \frac{300}{9} = \frac{100}{3}\text{ g}$$

19. (d) $\frac{t_{(gas)}}{t_{(O_2)}} = \sqrt{\frac{M_{(gas)}}{M_{(O_2)}}}$

$\Rightarrow \quad \frac{40}{16} = \sqrt{\frac{M_{(gas)}}{32}}$

$\Rightarrow \quad \frac{5}{2} = \sqrt{\frac{M_{(gas)}}{32}} \qquad \Rightarrow \frac{25}{4} = \frac{M_{(gas)}}{32}$

$\Rightarrow \quad M_{(gas)} = 200$ g/mol.

20. (a)

Rate of effusion ∝ Area of cross-section

$\therefore \quad \frac{r_A}{r_B} = \frac{A_A}{A_B} = \frac{\pi r^2}{r^2} = \frac{\pi}{1}$

21. (c) M. wt. of $C_nH_{2n+2} = 12n + 2n + 2$

$= 14n + 2 = 2(7n + 1)$

From $r \propto \frac{1}{\sqrt{M}}$

$\Rightarrow \quad \frac{1}{6} = \sqrt{\frac{2}{2(7n+1)}}$

$\Rightarrow \quad 36 = 7n + 1 \qquad \Rightarrow n = 5$

$\therefore \quad C_nH_{2n+2} = C_5H_{12}$

DPP 4.4

Subjective Type

1. $u_{rms} = \sqrt{\frac{n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + \cdots}{n_1 + n_2 + n_3 + \cdots}}$

$$= \sqrt{\frac{5 \times (15 \times 10^2)^2 + 10 \times (5 \times 10^2)^2 + 15 \times (10 \times 10^2)^2}{5 + 10 + 15}}$$

$= 9.79 \times 10^2$ m sec^{-1}

Also, $u_{AV} = \frac{n_1u_1 + n_2u_2 + n_3u_3 + \cdots}{n_1 + n_2 + n_3 \cdots}$

$$= \frac{(5 \times 15 \times 10^2) + (10 \times 5 \times 10^2) + (15 \times 10 \times 10^2)}{5 + 10 + 15}$$

$= 9.17 \times 10^2$ m sec^{-1}

2. Given, $P = 7.57 \times 10^3$ Nm^{-2}, $V = 1$ litre $= 10^{-3}$ m^3

$R = 8.314$ J, $n = \frac{2 \times 10^{21}}{6.023 \times 10^{23}}$ mole

Using $PV = nRT$.

$$7.75 \times 10^3 \times 10^{-3} = \frac{2 \times 10^{21}}{6.023 \times 10^{23}} \times 8.314 \times T$$

$\therefore \quad T = 274.2$ K

$$u_{rms} = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 274.2}{28 \times 10^{-3}}\right)} \qquad \text{(M in kg)}$$

$= 494.22$ m sec^{-1}

Now, $\frac{u_{MP}}{u_{rms}} = 0.82$

$\therefore \quad u_{MP} = 405.26$ m sec^{-1}

3. Let the u_{rms} of He and SO_2 be u_1 and u_2 respectively.

(i) For He: $u_1 = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3RT}{4}\right)}$

For SO_2: $u_2 = \sqrt{\left(\frac{3\,RT}{M}\right)} = \sqrt{\left(\frac{3RT}{64}\right)}$ (temp. is same)

$\therefore \quad \frac{u_1}{u_2} = 4$

(ii) Given, u_{rms} of $SO_2 = \frac{1}{2} u_{rms}$ of He

$\therefore \quad \sqrt{\left(\frac{3RT}{64}\right)} = \frac{1}{2}\sqrt{\left(\frac{3R \times 300}{4}\right)}$ ($T = 300$ K for He)

$\therefore T = 1200$ K

(iii) Since speed is independent of P and V terms and thus no effect on speed by changing volume.

(iv) Since u_{rms} is independent of no. of molecules and thus, no effect on speed by changing no. of molecules.

4. Let mass of mist particle be m, then K.E. of this particle $= \frac{1}{2}mu^2$, where u is rms velocity.

Also K.E. per molecule $= \frac{3RT}{2 \times N}$

Therefore $\frac{1}{2}mu^2 = \frac{3RT}{2 \times N}$

$$u = \sqrt{\left[3\frac{R}{N} \times \frac{T}{m}\right]}$$

$\because \quad m = 10^{-2}$ g; $R = 8.31 \times 10^7$ reg, $T = 300$ K

$$\therefore \quad u = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{6.023 \times 10^{23} \times 10^{-12}}} = 0.35 \text{ cm sec}^{-1}$$

5. According to Maxwell's molecular speed distribution:

$$\frac{n_g}{\Sigma n_g} \propto \frac{1}{u_{\text{rms}}}$$

$$\therefore \quad u_{\text{rms}} \propto \frac{\Sigma n_g}{n_g} \propto \frac{N}{n_g} \quad (\because \text{1 mole of both gases})$$

$$u_{\text{rms}\ Ar} \propto \frac{N}{n_{Ar}},\ u_{\text{rms}\ He} \propto \frac{N}{n_{\text{He}}}$$

$$\therefore \quad \frac{n_{\text{He}}}{n_{\text{Ar}}} = \frac{u_{\text{rms Ar}}}{u_{\text{rms He}}} = \frac{467}{1477} = 0.316$$

Single Correct Answer Type

6. (a) We know that $(pV_m)_{p \to 0} = 22.414$ L atm = (22.414 bar dm^3)

7. (c) We have $pV = \frac{1}{3} mN\overline{u^2} = \frac{2}{3} N\left(\frac{1}{2} m\overline{u^2}\right) = \frac{2}{3} N\overline{E}$

8. (a) $u_{rms} : u_{av} : u_{mp} :: \sqrt{3} : \sqrt{56/22} : \sqrt{2}$

9. (b) $u_{mp} = \sqrt{RT/M} \Rightarrow \sqrt{2R/M} = u_{mp}/\sqrt{T} = (0.3 \text{ m s}^{-1})/(300 \text{ K})^{1/2}$

$$u_{av} = \sqrt{8RT/\pi M} = (\sqrt{2R/M})(2\sqrt{T/\pi})$$
$$= [(0.3 \text{ m s}^{-1})/(300 \text{ K})^{1/2}][2(1200 \text{ K}/3.14)^{1/2}]$$

10. (c) The root mean square speed of gaseous molecules is given by

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\,pV_m}{M}}.$$

The choice (c) is correct. The root mean square speed varies as $\sqrt{p/\rho}$ and not on $\sqrt{p}$ and $\sqrt{1/\rho}$ as the ratio p/ρ remains constant at a given temperature.

11. (c) The average kinetic energy of gaseous molecules is independent of the nature of the gas.

12. (b) Let a g of Ne and b g and b of Ne and Ar be present respectively:

$$a + b = 30 \qquad (1)$$

$$\text{K.E. of mixture} = \frac{3}{2}\left[\frac{a}{20} + \frac{b}{40}\right]RT = 3 \times 10^3$$

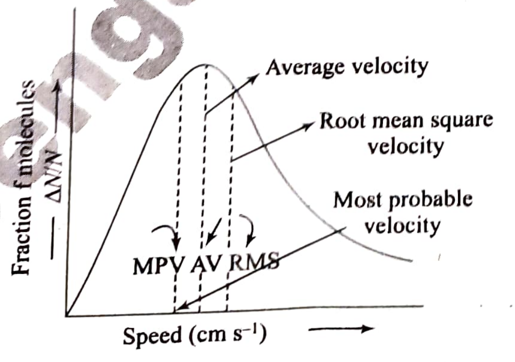
$$\frac{a}{20} + \frac{b}{40} = \frac{3 \times 10^3 \times 2}{3 \times 8.314 \times 250} = 0.96$$

$$\therefore \quad 2a + b = 38.48 \qquad (2)$$

$$\therefore \quad a = 8.48 \text{ and } b = 21.52$$

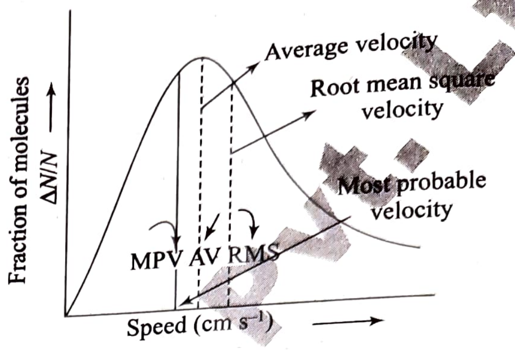
$$\therefore \quad \%\, b \text{ (i.e., Ar)} = \frac{21.52}{30} \times 100 = 71.7\%$$

13. (c)



The most probable speed may be defined as the speed possessed by the maximum fraction of molecules at a particular temperature.

14. (a)



Multiple Correct Answers Type

15. (b, c, d)

(a) Mean square speed is given by $\overline{u^2} = 3RT/M = 3kT/M$

(c) The expression of viscosity is $\eta = (mkT)^{1/2}/\pi^{3/2}\,\sigma^2$

16. (a, b, c)

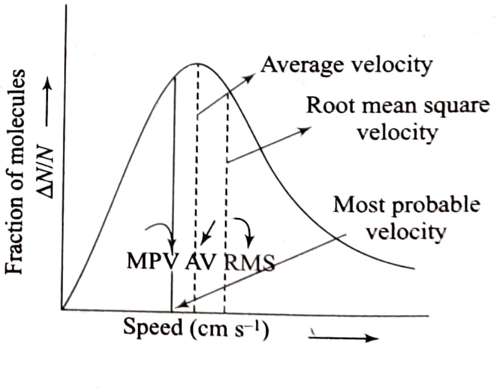
(a) The correct expression is $pV = (1/3)\ mN\overline{u^2}$ that is, it involves mean square speed and not square of mean speed.

(b) $\overline{u^2}$ stands for man square speed whereas $\overline{u}^2$ stands for square of mean speed.

(c) The expression of density is $\rho = Mp/RT$
Thus, density decreases with increase in temperature at constant pressure. The qualitative explanation that increase in temperature causes increase in volume, hence decrease in density (= mass/volume).

(d) According to kinetic theory of gases. $\overline{KE} = (3/2)RT$

17. (a, b)



18. (c, d)

The expressions of u_{av}, u_{rms} and u_{mp} are

$$u_{\text{av}} = \sqrt{\frac{8RT}{\pi m}};\ u_{\text{rms}} = \sqrt{\frac{3RT}{m}};\ u_{\text{mp}} = \sqrt{\frac{2RT}{m}}$$

From these, it follows that $u_{\text{mp}} < u_{\text{av}} < u_{\text{rms}}$

The average kinetic energy of gaseous atom is

$$\overline{E} = \frac{1}{2} mu_{\text{rms}}^2 = \frac{1}{2} m\left(\frac{3}{2} u_{\text{mp}}^2\right) = \frac{3}{4} mu_{\text{mp}}^2$$

Matching Column Type

19. (a → p, q, r), (b → s), (c → p, q, r), (d → s)
Molecular velocities increase with increase in temperature or with decrease in density. Molecular velocities do not change by changing pressure or volume at constant temperature.

Integer Type

20. (2) $u_{av} = \sqrt{\frac{8RT}{\pi M}}$, $T = 100$ K; $M = 529.5$ g mol^{-1}

$$= \sqrt{\frac{8 \times 8.314 \times 100}{3.14 \times 529.5}} = 2$$

∴ Average speed of molecule is 2.

21. (6)
Root mean square speed (c)

$$= \sqrt{\frac{\Sigma n_i v_i^2}{\Sigma n_i}} = \sqrt{\frac{10 \times 4^2 + 20 \times 7^2 + 40 \times 8^2}{10 + 20 + 40}}$$

$$= \sqrt{\frac{160 + 980 + 2560}{70}} = 7.27 \text{ m s}^{-1}$$

Most probable speed (c*) = 0.816 × c = 0.816 × 7.27 m s^{-1}
= 5.93 ≈ 6 m s^{-1}

Comprehension Type

22. (d) K.E. does not depend upon the nature of the gas.

23. (a) KE of n moles $= \frac{3}{2}nRT$

$(KE)_{He} = (KE)_{Ar}$

$$\frac{3 \times 0.3 \times R \times T}{2} = \frac{3 \times 0.4 \times R \times 400}{2}$$

$T = 533.3$ K

24. (b) $\overline{KE} = \frac{3RT}{2N_0} = \frac{3 \times 8.3143 \times 298}{2 \times 6.02 \times 10^{23}} = 6.17 \times 10^{-27}$ J

25. (a) $KE = \frac{3}{2}nRT = \frac{3}{2}pV$

∴ KE per unit volume $= \frac{KE}{V} = \frac{3}{2}p$.

DPP 4.5

Subjective Type

1. Pressure correction $= \frac{n^2 a}{V^2} = \frac{(4.4)^2 \times 3.6}{(44)^2 \times 1 \times 1}$ $\left(n = \frac{4.4}{44}\right)$
$= 0.036$ atm

Volume correction $= nb = \frac{4.4}{44} \times 0.04 = 0.004$ litre

2. ∵ $b = 4N \times v$ [where v is volume of 1 molecule (of steam)]
∴ Volume of 1 mole of steam

$$= \frac{b}{4} = \frac{0.0305}{4} \text{ litre} = \frac{0.0305}{5} \times 10^3 \text{ mL} = 7.625 \text{ mL}$$

Also, volume of 1 mole of $H_2O(l) = \frac{18}{0.958}$ mL

$$\therefore \frac{\text{Volume of 1 mole steam}}{\text{Volume of 1 mole } H_2O} = \frac{7.625 \times 0.958}{18} = 0.4058$$

∴ Volume of 1 mole of steam = 40% of volume of 1 mole of H_2O.

3. Given, $n = 5$; $V = 1$ litre; $T = 47 + 273 = 320$ K
$a = 3.592^\circ$; $b = 0.0427$
Using van der Waals' equation for n moles.

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\left[P + \frac{25 \times 3.592}{1}\right][1 - 5 \times 0.0427] = 5 \times 0.0821 \times 320$$

∴ $P = 77.218$ atm

4. Compressibility factor $(Z) = \frac{PV}{nRT}$

$$Z = \frac{40 \times 0.4}{1 \times 0.0821 \times 300} = 0.65$$

Since, Z value is lesser than 1 and thus, $nRT > PV$. In order to have $Z = 1$, volume of CO_2 must have been more at same P and T or CO_2 is more compressible than ideal gas.

5. For real gas, $PV = Z \cdot nRT = \frac{Z \cdot wRT}{M}$
Given compressibility factor $Z = 0.927$, $T = 273$ K, $P = 100$ atm, $V = 100$ litre

$$\therefore 100 \times 100 = 0.927 \times \frac{w}{30} \times 0.0821 \times 273$$

$w = 14.439 \times 10^3$ g
$= 14.439$ kg

Single Correct Answer Type

6. (d) At Boyle temperature, $Z = 1$ over wide range of pressure. This is due to the fact that effects produced by constants a and b compensate each other.

7. (d) The van der Waals constant b is four times the molecular volume of one mole of a gas.

8. (c) The value of $p_c V_c / RT_c$ is 3/8.

9. (a) $\left[P + \frac{a}{V^2}\right][V - b] = RT$

$$\therefore \left[P + \frac{a}{V^2}\right]V = RT \quad (b \text{ is negligible})$$

or $V^2 P - RTV + a = 0$

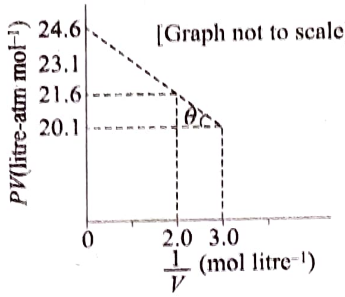
$$V = \frac{+RT \pm \sqrt{R^2T^2 - 4Pa}}{2P}$$

Since, V is constant at given P and T, V can have only one value or discriminant = 0.

$\therefore \quad R^2T^2 = 4\,Pa$

or $\quad a = \dfrac{R^2T^2}{4P} = \dfrac{(0.0821)^2 \times (273)^2}{4 \times 34.98} = 3.59 \text{ dm}^6 \text{ atm mol}^{-2}$.

10. (c)



van der Waals equation for 1 mol of real gas is

$$\left[P + \frac{a}{V^2}\right][V - b] = RT$$

Given that $b = 0$.

$$\therefore \quad \left(P + \frac{a}{V^2}\right)(V) = RT$$

$$\therefore \quad PV = RT - \frac{a}{V} \qquad \text{(i)}$$

Following $y = mx + c$ for the curve PV vs $\dfrac{1}{V}$.

Slope $= -a$

$$\text{Slope } = \frac{21.6 - 20.1}{2 - 3} = -1.5$$

$\therefore a = 1.5$

Multiple Correct Answers Type

11. (a, b, d)

(a) If nb is neglected in the van der Waals equation, we get $(p + n^2a/V^2)V = nRT \Rightarrow Z = pV/nRT = 1 - na/VRT$

(b) Since $pV = nRT$, the term pV is dependent on temperature. If na/V^2 is neglected in the van der Waals equation, we get

$$p(V - nb) = nRT \Rightarrow Z = \frac{pV}{nRT} = 1 + \frac{pp}{RT}$$

(c) The excluded volume is four times the volumes of molecules of 1 mol of a gas.

12. (a, b, c, d)

All statements are facts.

13. (a, b, d)

The unit of van der Waals constant b in SI units is $\text{m}^3 \text{ mol}^{-1}$.

14. (a, b, d)

At high pressure, V is so small that b cannot be neglected in comparison to V. The factor a/V^2 is no doubt large, but as P is very high, a/V^2 can be neglected in comparison to P.

15. (a, c)

Real gases have volume and force of attraction.

16. (a, c)

$\left(P + \dfrac{an^2}{V^2}\right)(V - nb) = nRT$, at high pressure $P >> \dfrac{an^2}{V^2}$.

Matching Column Type

17. (a → p), (b → p), (c → q, r), (d → s)

At very high pressure, van der Waals equation (for 1 mol gas) reduces to $PV = RT + Pb$. In this condition, attraction force among gas molecules will be negligible.

At high temperature and low pressure, real gases behave like ideal gas and obey ($PV = nRT$). For ideal gases $Z = 1$.

At normal temperature and pressure, the real gases obey van der Waals' equation of state, i.e., $\left(P + \dfrac{an^2}{V^2}\right)(V - nb) = nRT$.

Integer Type

18. (1) $Z_{(\text{ideal gas})} = \dfrac{V_m}{V_{\text{ideal}}} = 1$

19. (4) $b = 4$ (volume of gas molecule)

$$\therefore \quad \frac{b}{\text{Volume of gas molecule}} = 4$$

Comprehension Type

20. (c) The unit of a is the same as that of the expression pTV_m^2, i.e., $\text{Pa K m}^6 \text{ mol}^{-2}$.

21. (b) The Berthelot's equation is $p = \dfrac{RT}{V_m - b} - \dfrac{a}{TV_m^2}$

This gives $\dfrac{pV_m}{RT} = \dfrac{V_m}{V_m - b} - \dfrac{a}{V_mRT^2} = \left(1 - \dfrac{b}{V_m}\right)^{-1} - \dfrac{a}{V_mRT^2}$

$$= 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots - \frac{a}{V_mRT^2}$$

$$= 1 + \frac{1}{V_m}\left(b - \frac{a}{RT^2}\right)^2 + \left(\frac{b}{V_m}\right)^2 + \cdots$$

The second virial coefficient is $B = b - \dfrac{a}{RT^2}$.

22. (c) At Boyle temperature $B = 0$. This gives $T_B = \sqrt{a/Rb}$.

DPP 4.6

Subjective Type

1. $T_C = \dfrac{8a}{27Rb}$ and $P_C = \dfrac{a}{27b^2}$

$$\therefore \quad \frac{T_C}{P_C} = \frac{8b}{R} \quad \text{or} \quad b = \frac{RT_C}{8P_C}$$

$$\therefore \quad b = \frac{0.0821 \times 303}{8 \times 72} = 0.043 \text{ litre mol}^{-1}$$

$a = 27\,P_C \times b^2 = 27 \times 72 \times (0.043)^2 = 3.59 \text{ litre}^2 \text{ atm mol}^{-2}$

2. According to law of corresponding state,

$$\left[P_r+\frac{3}{V_r^2}\right][3V_r-1]=8RT_r$$

$$\left[P_r+\frac{3}{(0.4)^2}\right][3\times 0.4-1]=8\times 0.7277$$

$\therefore P = 10.350$

3. Inversion temperature,

$$T_i=\frac{2a}{R\cdot B}=\frac{2\times 0.246}{0.0821\times 0.0267}=224.4\text{ K}$$

Boyle temperature,

$$T_b=\frac{a}{R\cdot b}=\frac{0.246}{0.0821\times 0.0267}=112.2\text{ K}$$

Single Correct Answer Type

4. (d) The dipole moment in molecule results in strong intermolecular forces and since $T_c=\frac{8a}{27R\cdot b}$; T_c is more for H_2O.

5. (c) Liquefaction of a gas is easier if it possesses high T_c and higher T_i.

6. (b) A derivation for mean free path of gas.

7. (b) $T_B=\frac{a}{R\cdot b}$; $T_c=\frac{a}{27R\cdot b}$

$$\frac{T_B}{T_c}=\frac{27}{8}$$

8. (b) μ = +ve for cooling effect and μ = –ve for heating effect.

9. (a) Lesser is the value of Z at a pressure, easy will be the liquefaction of the gas. $Z < 1$ shows the dominance of attractive forces.

Multiple Correct Answers Type

10. (a, d)

The expression of mean free path is

$$\lambda = 1/\sqrt{2}\,\pi\sigma^2 N^* \text{ where } N^* = \pi/kT.$$

Hence, $\lambda = kT/\sqrt{2}\,\pi\sigma^2 p.$

11. (a, c)

(b) The molar heat capacity of diatomic molecules is $2.5R$. There is no contribution from vibrational motion.

(d) The average vibrational energy of a diatomic molecule is kT, because both kinetic energy and potential energy contribute.

12. (b, d)

The value of C_p/C_V for one mole of an ideal (monatomic) gas is equal to 5/3. The value of γ (= ratio of heat capacities) of gases decreases with increases in the atomicity of gaseous molecule.

Matching Column Type

13. (a → p, r), (b → q), (c → p, s), (d → q, r)

(a) For liquefaction of gas $T < T_C$ and $P > P_C$

(b) Above critical temperature gas cannot be liquefied.

(c) For condensation of vapour $T < T_C$ and $P < P_C$.

(d) For supercritical fluid $T > T_C$ and $P > P_C$.

Integer Type

14. (2) Inversion temperature $(T_i) = \frac{2a}{Rb}$

Boyle's temperature $(T_b) = \frac{a}{Rb}$

$$\therefore \frac{T_i}{T_b} = 2.$$

Comprehension Type

15. (b) $b = V_c/3$

16. (a) $a = 27(RT_c)^2/64p_c$

17. (c) $p_cV_c/RT_c = 3/8$

DPP 4.7

Subjective Type

1. We have

T_1 = 80.75°C ≡ 353.9 K; p_1 = 760 mm Hg;

T_2 = 25°C ≡ 298.15 K; p_2 = ?

Using the expression

$$\log\frac{p_2}{p_1}=-\frac{\Delta_{vap}H_m}{2.303R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

We get

$$\log\left(\frac{p_2}{\text{mm Hg}}\right)=$$

$$\log(760)-\frac{30.08\times10^3\text{ J mol}^{-1}}{(2.303)(8.314\text{ J K}^{-1}\text{ mol}^{-1})}\left[\frac{1}{298.15\text{ K}}-\frac{1}{353.9\text{ K}}\right]$$

This gives p_2 = 112.4 mm Hg.

2. Using the expression

$$\gamma_1=\left(\frac{\rho_1}{\rho_w}\frac{n_w}{n_1}\right)\gamma_w$$

We get $\gamma_1=\left(\frac{0.86}{0.996}\frac{20}{60}\right)(72.75\times10^{-3}\text{ N m}^{-1})$

$$= 20.94\times10^{-3}\text{ N m}^{-1}.$$

3. Using the expression $\eta = A\exp(E_a/RT)$, we get

$$\log\frac{\eta_1}{\eta_2}=\frac{E_a}{2.303}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Hence

$$\log\left(\frac{2.33}{2.84}\right)=\frac{E_a}{(2.303)(8.314\text{ J K}^{-1}\text{ mol}^{-1})}\left[\frac{1}{293\text{ K}}-\frac{1}{273\text{ K}}\right]$$

This gives

$$E_a = -\frac{\log(2.33/2.84)(293\text{ K})(273\text{ K})\,(2.303)(8.314\text{ J K}^{-1}\text{mol}^{-1})}{(20\text{ K})} = 6583\text{ J mol}^{-1}$$

For 60°C, we will have

$$\log\left(\frac{\eta_1}{2.84}\right) = \frac{(6583\text{ J mol}^{-1})}{(2.303)(8.314\text{ J K}^{-1}\text{mol}^{-1})}\left[\frac{1}{333\text{ K}} - \frac{1}{273\text{ K}}\right]$$

This gives $\eta_2 = 1.69$ millipoise.

4. Trouton's rule may be expressed as:

$$\frac{\Delta H_{\text{vap}}}{T_b} = 88\text{ J mol}^{-1}\text{K}^{-1}$$

$$\therefore\quad \Delta H_{\text{vap}} = (88\text{ J mol}^{-1}\text{ K}^{-1})(309\text{ K})$$

$$= 27192\text{ J mol}^{-1} = 27.192\text{ kJ mol}^{-1}$$

5. The surface area of the spherical drop of radius 3.0 mm

$$= 4\pi r_1^2$$
$$= 4\pi(3.0 \times 10^{-3}\text{ m})^2 = 1.13 \times 10^{-4}\text{ m}^2$$

The surface area of spherical drop of radius 3.0×10^{-3} mm = $4\pi r_2^2$

$$= 4\pi(3.0 \times 10^{-6}\text{ m})^2 = 1.13 \times 10^{-10}\text{ m}^2$$

The number of drops of radius 3×10^{-3} mm that can be formed from one drop of radius 3 mm

$$= \frac{\text{Volume of bigger drop}}{\text{Volume of smaller drop}}$$

$$= \frac{(4/3)\pi\,(3.0\text{ mm})^3}{(4/3)\pi(3.0 \times 10^{-3}\text{ mm})^3} = 1.0 \times 10^9$$

The total surface area of all the small drops = $(1.13 \times 10^{-1}\text{ m}^2)(1.0 \times 10^9) = 1.13 \times 10^{-1}\text{ m}^2$

Increase in surface area = $(1.13 \times 10^{-1}\text{ m}^2) - (1.13 \times 10^{-4}\text{ m}^2)$

$$= 1.13 \times 10^{-4} \times 999\text{ m}^2$$

$\therefore$ Work done in dispersion = surface tension × increase in surface area

$$= (72.8 \times 10^{-3}\text{ J m}^{-2})(1.13 \times 999 \times 10^{-4}\text{ m}^2) = 8.2 \times 10^{-3}\text{ J}$$

6. If 'w' is the minimum work required to stretch the surface area by an amount A, then

$$w = \gamma A = (72.8\text{ dynes cm}^{-1})(3.0\text{ cm}^2)$$
$$= 218.4\text{ dynes cm} = 218.4\text{ ergs.}$$

Single Correct Answer Type

7. (c) The correct expression is

$$\log p = \frac{\Delta_{\text{vap}} H_m}{2.303R} \cdot \frac{1}{T} + \text{constant}$$

8. (d) The surface tension and surface energy has the same numerical value.

9. (a) The surface tension of water increases when sodium chloride is dissolved in it.

10. (d) The viscosity of a gas increases with increase in temperature.

11. (c) The variation of viscosity of a liquid varies with temperature. The governing expression is

$$\eta = A\exp(-E/RT).$$

12. (c) With increase of temperature, the kinetic energy of the molecules of liquid increases which can overcome the intermolecular forces. Hence, the liquid starts flowing.

In other words, the viscosity of a liquid decreases with increase in temperature. It has been found that the decrease is about 2% per degree rise in temperature.

13. (b) The surface tension of liquids generally decreases with increase of temperature and becomes zero critical temperature. The decrease in surface tension with increase of temperature is obviously due to the fact that with increase of temperature, the kinetic energy of the molecules increases and therefore, the intermolecular attraction decreases.

Integer Type

14. (8) $\dfrac{h_A}{h_B} = \dfrac{\gamma_A/\rho_A}{\gamma_B/\rho_B} = \dfrac{\gamma_A\rho_B}{\gamma_B\rho_A} = \left(\dfrac{1}{2}\right)\left(\dfrac{1}{2}\right) = \dfrac{1}{4}$

$$h_B = 4h_A = 4 \times 2.0\text{ cm} = 8.0\text{ cm}.$$

15. (7) $h = \dfrac{2\gamma}{r\rho g} = \dfrac{2 \times 72.8}{(0.0211\text{ cm})(1\text{ g cm}^{-3})(981\text{ cm s}^{-2})}$

$= 7.034\text{ dynes s}^2\text{ g}^{-1} \approx 7\text{ cm}$ (dynes = g cm s^{-2})

CHAPTER 5

DPP 5.1

Subjective Type

1. The given diagram represents that the process is carried out in infinite steps, hence it is an isothermal reversible expansion of the ideal gas from pressure 2.0 atm to 1.0 atm 298 K.

$$W = -2.303\, nRT \log \frac{p_1}{p_2}$$

$$W = -2.303 \times 1 \text{ mol} \times 8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 298 \text{ K} \log 2 \qquad \left(\because \frac{p_1}{p_2} = \frac{2}{1}\right)$$

$$W = -2.303 \times 1 \times 8.314 \times 298 \times 0.3010 \text{ J}$$

$$W = -1717.46 \text{ J}$$

2. Efficiency of cycle $= \dfrac{\text{Area of closed cycle}}{\text{Area under the curve}} \times 100$

$$= \frac{\frac{1}{2} \times (1500-1000) \times (250-150)}{\frac{1}{2} \times (1500-1000) \times (250-150) + (1500-1000) \times (150-0)} \times 100$$

$$= \frac{\frac{1}{2} \times 500 \times 100}{\frac{1}{2} \times 500 \times 100 + 500 \times 150} \times 100$$

$$= \frac{500 \times 50 \times 100}{500 \times 50 + 500 \times 150} = 25$$

3. Initially for N_2

$$25 \times V_1 = \frac{28}{28} \times 0.0821 \times 350$$

$V_1 = 1.1494$ L

Finally for N_2

$$1 \times V_2 = \frac{28}{28} \times 0.0821 \times 350$$

$\Rightarrow \quad V_2 = 28.735$ L

$\therefore$ Work is done against constant external P.

$\therefore$ Irreversible

Hence $W = -P\Delta V$

$= -1 \times (28.735 - 1.1494)$

$= -27.5856$ L atm $= -27.5856 \times 101.3$

$= -2794.973$ J

Now $q = \Delta U - W$

$= 0 - (-2794.973)$

$\{\because \Delta U = 0$ For isothermal process$\}$

$= 2794.973$ J

4. $W = 2.303\, nRT \log_{10} \dfrac{v_2}{v_1}$

or $\quad 2.303\, nRT \log_{10} \dfrac{P_1}{P_2}$

$T = 300$ K

$n = 1$ mole

$P_1 = 10$ atm

$P_2 = 2$ atm

$W = 2.303 \times 1 \times .082 \times 300 \times \log_{10} 5$

$= 39.65$ L-atm

$\simeq 39.65 \times 101.3$ J

$\simeq 4017.32$ Joule

From question, this amount will be equal to *mgh*.

$\Rightarrow \quad 4017.32 = m \times 9.8 \times 1$

$\Rightarrow \quad m = 409.93$

5. **(a)** Final temperature

$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$300 \times V^{\gamma-1} = T_2 (2V)^{\gamma-1}$

$\dfrac{300}{T_2} = 2^{\gamma-1}$

$\dfrac{300}{T_2} = 2^{1.66-1}$

$\dfrac{300}{T_2} = 2^{.66}$

$\dfrac{300}{T_2} = 2^{2 \times .33} = 2^{2 \times \frac{1}{3}}$

$300 = T_2 . 2^{2/3}$

$T_2 = 189$ K

(b) Change in internal energy

$dU = nc_v\, dT$

$= 2 \times \dfrac{5}{2} \times 8.314 \times 111$

$= 4614.27$ J

(c) Work done by gas

$\Delta U = Q + w$

As $Q = 0$

$\therefore \Delta U = w$ i.e., -2767 J

6. $\Delta H = 30.84$ kJ/mole

$PV = nRT \quad \Rightarrow \quad 1 \times V_2 = 1 \times 0.082 \times 353$

$\Rightarrow \quad V_2 = (0.082 \times 353)$ Lit.

As initial volume is negligible, so $\Delta H = \Delta E + P_2 V_2$

$\Delta E = 27.91$

$Q = i \times t = (0.5 \times t)$

Energy $= Q \times V = 0.5 \times t \times V = 0.5 \times 12 \times t = 6t$

$6t = 30.84 \times 1000 \times 0.1$

$t = 514$ sec.

7. (i) Beaker is open and in open beaker external pressure remains constant.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2(g)$$

$$\frac{130}{65} = 2 \text{ mole}$$

$$PV = nRT$$

$$P\Delta V = n_gRT$$

$$W = -n_gRT = 2 \times 2 \times 300 = -1200 \text{ cal.}$$

(ii) $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2(g)\uparrow$; $\Delta H = -45$ J/mole

$$H_2O\ (l) \longrightarrow H_2O(g); \quad \Delta H = 2250 \text{ J/mole}$$

Total heat lost = Total heat gain

$$45 \times 2 = n \times 2250 \quad \Rightarrow \quad n = 0.04 \text{ mole} = 0.72 \text{ gram}$$

$$W = -n_gRT = 0.04 \times 2 \times 300 = -24 \text{ cal}$$

$$W_{\text{total}} = -1200 - 24 = -1224 \text{ cal}$$

Single Correct Answer Type

8. (a) $W = -P(V_2 - V_1)$

$= -1 \times 35 = -35$ L-atm

$= -35 \times 101.3$ J $= -3545.5$ J

$$= -\frac{3545.5}{4.18} = 848.2 \text{ cal}$$

9. (c) From first law of thermodynamics, we have $dU = dq + dw$. For adiabatic expansion, $dq = 0$. Hence $dU = dw$ or $nC_{V,m}\,\Delta T$

$$= -p\Delta V \Rightarrow \Delta T = -\frac{p_{\text{ext}}\Delta V}{nC_V, \text{m}}$$

i.e. $$T_f = T - \frac{(1 \text{ atm})\,(2\text{L})}{(1 \text{ mol})(1.5 \times 0.082\text{L atm K}^{-1}\text{mol}^{-1})}$$

$$= T - \frac{2\text{K}}{1.5 \times 0.082}$$

10. (a) The work done during the cyclic path is equal to the area enclosed by the path, which is pV.

Work done

$= (2p - p)(2V - V)$

$= pV$

11. (b) For an adiatomic process, pV^{γ} = constant. Also γ $(= C_{p,m}/C_{V,m})$. For a diatomic gas $(= 7/5)$ is smaller than that of a monatomic gas $= (5/3)$. Hence, for given volume. $(V^{\gamma})_{\text{diatomic gas}} < (V^{\gamma})_{\text{monatomic gas}}$

Since at any instant, pV = constant. We will have $p_{\text{diatomic gas}} > p_{\text{monatomic gas}}$

Hence, the curve 1 is meant for a diatomic gas and the curve 2 for a monatomic gas.

12. (d) Internal energy change in cyclic process is zero.

13. (b) $W_{\text{rev}} = -2.303\, nRT \log \dfrac{V_2}{V_1}$

$$= -2.303 \times 1 \times 0.0821 \times 298 \log \frac{20}{10}$$

$= -2.303 \times 0.0821 \times 298 \times \log 2$ L atm

or $W_{\text{rev}} = -2.303 \times 8.314 \times 298 \times \log 2$ J

$= -2.303 \times 8.314 \times 10^7 \times 298 \times \log 2$ erg.

14. (a) $w = -nR\,\Delta T = -2 \times 8.314 \times 100 = -1662.8$ J

$$\Delta U = n\int_{300}^{400} (20 + 10^{-2}T)\text{dT}$$

$$= 2\left[2 \times 100 + \frac{10^{-2}}{2}(400^2 - 300^2)\right] = 4700 \text{ J}$$

$4700 = q - 1662.8$

$\therefore \quad q = 6362.8$ J

15. (d) $w = -P_{\text{ext}}.\Delta V = -\Delta n_gRT$ and Δn_g is –ve for I and II.

Also ΔV = –ve for IV

Multiple Correct Answers Type

16. (a, c, d)

(a) $T_1 = T_2$ as the process is isothermal. So, (a) is correct.

(b) $T_3 < T_1$ because cooling takes place on adiabatic expansion. So, (b) is incorrect.

(c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$ because area under the isothermal curve. So, (c) is correct.

(d) $\Delta U_{\text{adiabatic}}$ = –ve because when adiabatic expansion occurs, internal energy decreases. Thus, $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$. So, (d) is correct.

17. (a, d)

Internal energy and molar enthalpy are state function.

18. (a, b, c)

For a cyclic process $dU = 0$

$\therefore \quad q = \Delta U + (-w),\ q = -w$

Also, w = area covered by sphere

$$= \pi r^2 = \pi \times \left[\frac{(V_2 - V_1)}{2}\right]^2 = \frac{\pi \times (20)^2}{2^2}$$

$= 100\pi = 100 \times 3.14$ J $= 314$ J

19. (a, b, c)

$$W = -P_{\text{ext}}\,(V_2 - V_1)$$

20. (a, b, c)

$$\Delta U = Q + W = 0 + \int -P_{\text{ext.}}\,dV = -P_{\text{ext}}\,(V_2 - V_1)$$

$$\Rightarrow C_V(T_2 - T_1) = -P_{\text{ext.}}\left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right);$$

Here $P_{\text{ext}} = P_2$.

$$\Rightarrow \quad \frac{5}{2}R\,(673 - 373) = -673R + \left(\frac{373R}{0.1013}\right)P_2$$

$$\Rightarrow \quad P_2 = 0.3865 \text{ MPa}$$

$\Delta U = C_v(T_2 - T_1)$ J/mole

$$= \frac{5}{2}R \times (673 - 373) \text{ J/mole}$$

$$= \frac{5}{2} \times R \times 300 = \frac{5}{2} \times 8.314 \times 300 \text{ J/mole}$$

$= 6235.50$ J/mole.

21. (a, b, c)

$\Delta U = Q + W \Rightarrow nC_v\,\Delta T = 0 + W$ (In adiabatic process $Q = 0$)

$$\Rightarrow \quad W = nCV(T_2 - T_1) \qquad \text{(i)}$$

$$= \frac{nR}{\gamma - 1}(T_2 - T_1) \quad \left\{\text{Since } C_V = \frac{R}{\gamma - 1}\right\}$$

$$= \frac{nRT_2 - nRT_1}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} \qquad \text{(ii)}$$

Again $W = -nC_V(T_1 - T_2) = -nC_V\left[1 - \frac{T_2}{T_1}\right]T_1$

$$\Rightarrow \quad W = -nC_V T_1\left[1 - \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}\right]$$

$$= -nC_V T_1\left[1 - \left(\frac{P_2}{P_1}\right)^{R/C_P}\right] \qquad \text{(iii)}$$

Matching Column Type

22. **(A→5), (B→4), (C→6), (D→1), (E→7, 11, 12), (F→2), (G→3), (H→10), (I→8), (J→9), (K→1, 12, 13), (L→7, 11)**

Correct matching can be done as:

A.	Adiabatic process	No transfer of heat
B.	Isolated system	No exchange of energy and matter
C.	Isothermal change	Constant temperature
D.	Path function	Heat
E.	State function	Internal energy
		Entropy
		Pressure
F.	$\Delta U = q$	At constant volume
G.	Law of conservation of energy	First law of thermodynamics
H.	Reversible process	Infinitely slow process which proceeds through a series of equilibrium states
I.	Free expansion	$p_{ext} = 0$
J.	$\Delta H = q$	At constant pressure
K.	Intensive property	Heat
		Pressure
		Specific heat
L.	Extensive property	Internal energy
		Entropy

Integer Type

23. (7) $W = -p_{ext}\,\Delta V$

$PV = nRT$

$W = -p_{ext}(V_f - V_i)$

$V_f - V_i \cong V_f$ as $V_i = 0$

$PV_f = nRT$

$$V_f = \frac{nRT}{p_{ext}}$$

$$W = p_{ext} \times \frac{nRT}{p_{ext}}$$

$= -.3125 \times .083 \times 273$

$= -7.08$

$\cong 7$

Comprehension Type

24. (a) At the start, $P = 1$ atm, $V = 10$ L, $T = 313$ K

$\therefore$ from $PV = nRT$

$$n = \frac{1 \times 10}{0.0821 \times 313} = 0.3891 \sim 0.39$$

25. (a) $W_{DAC} = W_{(D\to A)} + W_{(A\to C)}$

$\therefore W_{D\to A} = 0 \qquad (\because \Delta V = 0)$

$\therefore W_{DAC} = W_{A\to C} = -p_{ext}\,\Delta V = -1(.50 - 10) = -1 \to -9.5$

$= 9.5$ L atm $= 962.54$ J

$= 0.96$ kJ

26. (b) For isothermal process

$\Delta T = 0$

$\therefore \quad \Delta E = 0$

$\Delta U = 0$

DPP 5.2

Subjective Type

1. $\Delta H = \Delta U + P\,\Delta V$

Here, $\Delta U = +0.21$ kJ mol^{-1} $= 0.21 \times 10^3$ J mol^{-1} $= 210$ J mol^{-1}

$P = 1$ bar $= 10^5$ Pa

ΔV = Molar volume of aragonite – Molar volume of calcite

$$= \frac{100}{2.93} - \frac{100}{2.71}\,\text{cm}^3\text{mol}^{-1}$$

$(\because$ Molar mass of $CaCO_3 = 100$ g mol$^{-1})$

$$= 100\left(\frac{1}{2.93} - \frac{1}{2.71}\right) = 100 \times \frac{-0.22}{2.93 \times 2.71}$$

$$= -2.77\,\text{cm}^3\text{mol}^{-1} = -2.77 \times 10^{-6}\,\text{m}^3\text{mol}^{-1}$$

$\therefore \quad \Delta H = 210 + 10^5(-2.77 \times 10^{-6}) = 210 - 0.277$ J

$= 209.72$ J mol^{-1}

2. Taking the initial volume as negligible (as no gaseous reactant is present), change in volume during expansion $(\Delta V) = 22.4$ L.

External pressure $(P_{ext}) = 1$ atm

$\Delta H = \Delta U + P\Delta V$ or $\Delta U = \Delta H - P\Delta V$

$P\Delta V = 1$ atm $\times 22.4$ L $= 22.4$ L atm $= 22.4 \times 101.3$ J $= 2307$ J

$= 2.31$ kJ

$\therefore \Delta U = -154.4 - 2.31 = -156.71$ kJ

3. $\Delta q = 0$; $\Delta W = 100 \times 1 = 100$ bar mL

$= 100 \times 10^5 \times 10^{-6}$ J $= 10$ J

or $\quad \Delta E = 10$ J

$\Delta H = \Delta E + \Delta PV = 10\text{ J} + (P_2V_2 - P_1V_1)$

or $\quad \Delta H = 10\text{ J} + 100 \times 99 - 100 \times 1$

$= 10$ J $+ 9800$ bar mL

or $\quad \Delta H = 10\text{ J} + 9800 \times 10^5 \times 10^{-6}\text{ J} = 990$ J

4. The enthalpy change for 0.8 g of water $= \Delta H'$(say)

$\therefore \quad \Delta H' = 0.5 \times 12 \times 300 = 1800$ J

$$\text{Per mole } \Delta H = \frac{1800}{\frac{0.8}{18}} = \frac{1800 \times 18}{0.8} = 40.5\text{ kJ/mol}$$

$\Delta E = \Delta H - RT = 40.5 - 8.314 \times 10^{-3} \times 373$
$= 40.5 - 3.1 = 34.4$ kJ/mole

Single Correct Answer Type

5. (b) Combustion of Benzene is represented by

$$C_6H_6(l) + \frac{15}{2} O_2 (g) \rightarrow 6CO_2 (g) + H_2O (l)$$

$$\Delta n = 6 - \frac{15}{2} = -\frac{3}{2}$$

From $\Delta H = \Delta U + \Delta n_g RT$

$\Delta H - \Delta U = \Delta n_g RT$

$$\Delta H - \Delta U = -\frac{3}{2} \times 8.314 \times 10^{-3} \times 300$$
$$= 3741.3 \times 10^{-3} = 3.741 \text{ kJ}$$

6. (c) For the reaction $CCl_4(l) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl(g)$, we have

$\Delta_g H = \Delta_f H\,(CO_2, g) + 4\Delta_f H\,(HCl, g) - \Delta_F H\,(CCl_4, 1) - 2\Delta_f H(H_2O, g)$
$= (-394 - 4 \times 93 + 107 + 2 \times 242)$ kJ mol^{-1}
$= -175$ kJ mol^{-1}
$\Delta H = \Delta U + \Delta n_g RT$
$\Delta U = \Delta H - \Delta n_g RT$
$= -175 - (3)(8.314 \times 10^{-3}$ kJ K^{-} mol^{-1}) (300 K)
$= -182.5$ kJ mol^{-1}

Multiple Correct Answers Type

7. (a, b, c)

When $\Delta H = \Delta U + \Delta n_g RT$ (i)

When $\Delta n_{(g)} = 0$, $\Delta H = \Delta U$ i.e., heat of reaction will be same at constant pressure and at constant volume.

8. (b, d)

Given $\Delta H = -670.48$ kcal mol^{-1}
$T = 25°C = 298$ K
$W = 46$ g
M.wt. = 40 g (C_2H_5OH)
$\therefore$ for
$C_2H_6O\ (l) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l)$
Ethanol
$\Delta n_g = 2 - 3 = -1$
Now, from $\Delta H = \Delta U + \Delta n_g RT$
$\Delta U = \Delta H - \Delta n_g RT$
$= -670.48 - (-1) \times (2 \times 10^{-3}) \times 298$
$= -669.88$ kcal
or $= -669.88 \times 10^3 \times 4.18$ J
$= -280.01 \times 10^4$ J

9. (a, b, c)

$\Delta H = \Delta U + P.\Delta V + V\Delta P + P\Delta V$ is correct relation.

10. (b, c)

Matching Column Type

11. (a → q), (b → p, r, s), (c → s), (d → p, q, r)

(a) → Bond breakage requires energy
(b) → Burning always releases energy
→ Bond formation releases

(c, d) → If $\Delta ng = 0$, then $\Delta H = \Delta U$.
If $\Delta ng \neq 0$, then $\Delta H \neq \Delta U$.

Integer Type

12. $q_p - q_v = \Delta n_g\ RT$

$$\therefore \Delta n_g = \frac{q_p - q_v}{RT} = \frac{5000 \text{ Jmol}^{-1}}{8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 300 \text{ K}}$$
$$= 2.0$$

13. $\Delta H - \Delta U = \Delta n_g RT$
$\Delta U - \Delta H = \Delta n_g RT$
$= -(-2)RT = 2RT$

Comprehension Type

14. (b) $\Delta U_1 = q_1 + w_1 = 5960 \text{ J} - 2200 \text{ J} = 3760 \text{ J}$;
$\Delta U_2 = q_2 + w_2 = -5585 \text{ J} + 825 \text{ J} = -4760 \text{ J}$;
$\Delta U_3 = q_3 + w_3 = -2980 \text{ J} + 1100 \text{ J} = -1880 \text{ J}$;
$\Delta U_4 = 3645 \text{ J} + w_4$
Since the process is cyclic, the net ΔU ($= \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4$) will be equal to zero.
Hence $3760 \text{ J} - 4760 \text{ J} - 1880 \text{ J} + (3645 \text{ J} + w_4) = 0$
This gives $w_4 = -765$ J.

15. (c) $\Delta U_{net} = 0$. See question 14.

16. (a) Steps 1 and 2 taken together will accompany with a net decrease in the internal energy of the gas.

17. (b) The reactions to be considered are:

$$C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g); \quad \Delta H^o = -110 \text{ kJ mol}^{-1}$$

$$C(s) + O_2\ (g) \rightarrow CO_2(g); \quad \Delta H^o = -395 \text{ kJ mol}^{-1}$$

If x is the amount of C giving CO, then
$[x(-110) + (1.0 \text{ mol} - x)(-395)]$ kJ mol^{-1} $= -315$ kJ

$$x = \frac{-315 + 395}{395 - 110} \text{mol} = \frac{80}{285} \text{mol} \simeq 0.28 \text{ mol}$$

Mass of C reacted to give CO = (0.28 mol)(32 g mol^{-1}) ≃ 9.0 g

18. (d) Amount of C yielding CO_2 = 1.0 mol − 0.28 mol = 0.72 mol
Mass of O_2 reacted yielding CO_2 = (0.72 mol) (32 g mol^{-1})
≃ 23 g

19. (a) Mass of O_2 reacted CO = $\left(\frac{0.28 \text{ mol}}{2}\right)$(32 g mol^{-1}) = 4.5 g

Mass of total O_2 reacted = 23 g + 4.5g = 27.5 g

DPP 5.3

Subjective Type

1. Given

$$C_2H_2 + \frac{5}{2} O_2 \rightarrow 2CO_2 + H_2O;$$

$\Delta H = -310.6$ kcal mol^{-1} (i)

and $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
$\Delta H^o = -337.2$ kcal mol^{-1} (ii)

and $H_2 + 1/2O_2 \rightarrow H_2O$;

$\Delta H^\circ = -68.3$ kcal mol^{-1}

Inverse of (ii)

$2CO_2 + 2H_2O \rightarrow C_2H_4 + 3O_2$;

$\Delta H^\circ = 337.2$ kcal mol^{-1}

(i) + (iii) + (iv) (iv)

$$C_2H_2 + \frac{5}{2}O_2 + H_2 + \frac{1}{2}O_2 + 2CO_2 + 2H_2O$$

$$\rightarrow 2CO_2 + H_2O + H_2O + C_2H_4 + 3O_2;$$

$$\Delta H = -310.6 + (-68.3) + 337.2$$

$$\Rightarrow \quad C_2H_2 + H_2 \rightarrow C_2H_4;\ \Delta H = -41.7 \text{ kcal mol}^{-1}$$

2. We will calculate the heat of formation (combustion) of acetylene for 3 moles.

Because 3 moles of C_2H_2 will participate in formation of 1 mole of C_6H_6.

i.e. Total enthalpy of combustion of 3 moles of C_2H_2

$= 3 \times -1297.25$ kJ

$= -3891.95$ kJ

and from equation (i)

The difference in enthalpy of reaction will be considered as enthalpy of polymerization.

$= -3891.95 - (-3344.48)$

$= -547.2$ kJ mol^{-1}

3. $2As(s) + \frac{3}{2}O_2(g) \rightarrow As_2O_3(s)$; $\Delta H_f\,(As_2O_3) = ?$

$\Delta H_f = -(i) + 2\,(ii) + 2\,(iii) - 6\,(iv) - 6(v) + 3\,(vi)$

$\Delta H_f = -7550 - 2 \times 71390 - 2 \times 17580 + 6 \times 17315 + 6 \times 22000$

$- 3 \times 68360 = -154.68$ kcal.

4. Amount of O_2 taken per day

$$= 500 \times \frac{5}{100} \times 20 \times 60 \times 24 \text{ ml}$$

$= 720$ litre

No. of moles of O_2 taken/day $= \frac{PV}{RT}$

$$= \frac{1 \times 720}{0.082 \times 300} = 29.27$$

$C_{12}H_{22}O_{11}\,(s) + 12O_2\,(g) \rightarrow 12\,CO_2(g) + 11H_2O(l)$

1 mole 12 mole $\Delta H = -3690$ J/mole

By 12 moles of O_2, heat liberated $= -3690$ J

$\Rightarrow$ By 29.27 moles of O_2, heat liberated

$$= \frac{29.27}{12} \times (-3690)\ \text{J} = 9000 \text{ J} = 9 \text{ kJ}$$

5. The reaction involved is: $Fe_2O_3(s) + 2Al \rightarrow Al_2O_3\,(s) + 2Fe(s)$

$\Delta H = \Delta_f H\,(Al_2O_3, s) - \Delta_f H\,(Fe_2O_3,s)$

$= (-1669 + 833)$ kJ/mol $= -836$ kJ/mol

Total mass of the reactants = Molar mass of $Fe_2O_3 + 2 \times$ (molar mass of Al)

$= 160 + 2 \times 27 = 214$ g

$\therefore$ Fuel value per gram of mixture $= \frac{836}{214} = 3.906$ kJ/g

$= 3906$ J/g

Total volume of the reactants

$$= \frac{160}{5.2} + 2 \times \frac{27}{2.7} = 50.77 \text{ cm}^3$$

$\therefore$ Fuel value per cm^3 of mixture $= \frac{836 \text{ kJ}}{50.77 \text{ cm}^3}$

$= 16.47$ kJ/cm^3

$= 16470$ Joules

Single Correct Answer Type

6. (b) Combustion of C_2H_4

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

$\Delta H_{comb.} = 1411$ kJ, When $n_{C_2H_4} = 1$ mol

or $\quad nO_2 = 3$ mol

If $\Delta H_{comb} = 6226$ kJ

Then $nO_2 = \frac{6226 \times 3}{1411}$ mole

$$= \frac{6226 \times 3 \times 22.4}{1411} = 296.5 \text{ L}$$

7. (b) From given

$H_2 + 1/2O_2 \rightarrow H_2O$; $\Delta H = -68.39$ kcal

$K + H_2O + \text{water} \rightarrow KOH(aq) + ½H_2$;

$\Delta H = -48$ kcal

KOH + water; $\Delta H = +14$ kcal

Thus, $K + 1/2H_2 + 1/2O_2 \rightarrow KOH$;

$\Delta H = -68.39 - 48.00 + 14.00$

8. (b) From the given data,

Only 0.2 moles of each of HNO_3 and KOH will be neutralized.

So, 1 mol of H_2O formation releases 57.0 kJ.

$\therefore$ 0.2 mol releases 57.0×0.2 kJ $= -11.4$ kJ

9. (d) From Hess's law

$\Delta H_{soln} = \Delta H_{l.E} + \Delta H_{hydration}$

$-25 = +67 + \Delta H_{hydration}$

$\Rightarrow \quad \Delta H_{hydration} = -92$ kJ

10. (b) $\Delta H^\circ_f\ C_2H_5OH\,(l) = -66$ kcal/mole

$\Delta H = -66$ kcal/mole (1)

$CH_3 - O - CH_3 + 3O_2 \rightarrow 2CO_2 + 3H_2O$

$\Delta H = -348$ kcal/mole (2)

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O$ $\quad \Delta H_3 - 68$ kcal/mole (3)

$C + O_2 \rightarrow CO_2$ $\quad \Delta H_4 = -94$ kcal/mole (4)

Target equation = –eq 1 – eq 2 + 3 eq 3 + 2 eq 2

$\Delta H = +66 + 348 - 3 \times 68 - 2 \times 94 = +66 + 348 - 204 - 188$

$\Rightarrow \Delta H = 22$ kcal/mole

$\Delta H = \Delta E + \Delta n_g RT \Rightarrow 22 = \Delta E + 1 \times 2 \times 298 \times 10^{-3}$

$\Rightarrow \Delta E = 21.4$ kcal/mole

11. (c) $\Delta H_{ionization} = \Delta H_{neutralization}$ of WA + SB – $\Delta H_{neutralization}$ of SA + SB

$= -56.1 - (-57.3) = 1.2$ kJ eq^{-1}

Enthalpy of ionization for making 100% ionization when there is no ionization at all = 1.5 kJ eq^{-1}

$\therefore$ % of ionization $= \frac{1.5 - 1.2}{1.5} \times 100 = 20\%$

Multiple Correct Answers Type

12. (a, c, d)

Cyclopropane is the most strained.

13. (a, b, d)

Stable state of 'C' is graphite.

14. (a, b)

(a) Generates $\frac{60 \times 0.1 \times 13.7}{1000}$ kcal heat which is used by 120 mL solution.

(b) Generates $\frac{30 \times 0.1 \times 13.7}{1000}$ kcal heat which is used by 60 mL solution.

15. (b, c)

$\Delta H_1^\circ = \Sigma H^\circ_{s.s.} - \Sigma H^\circ_R$ and so on.

16. (a, b, c, d)

All are exothermic

17. (a, c)

$e_{Cl-Cl} > e_{F-F}$

Matching Column Type

18. (a → r, q), (b → p, q), (c → s, q), (d → q)

Enthalpy of combustion of CO: It is defined as the enthalpy change when one mole of CO combines with the requisite amount of oxygen to give products in their stable forms.

Standard enthalpy of formation: The standard enthalpy change for the formation of one mole of compound from its element in their most stable states of aggregation is called standard molar enthalpy of formation.

Enthalpy of reaction: The standard enthalpy of a reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

Integer Type

19. (8) 0.4 M H_2SO_4 contains 0.8 mol L^{-1} of H^+ ions while 0.1 M HCl contains 0.1 mol L^{-1} of H^+ ions. Hence, enthalpy of neutralization of 0.4 M H_2SO_4 will be 8 times that of 0.1 M HCl.

20. (6) $\Delta H = \Delta_f H$ (products) $-\Delta_f H$ (reactant)

$= -350.6 + 128.3 + 216.3$

$= -6$ kcal

Comprehension Type

21. (a) **Heat of formation:** The heat change for the formation of one mole of compound from its element in their most stable states of aggregation is called heat of formation.

22. (c) **Enthalpy of combustion:** It is defined as the enthalpy change when one mole of compound combines with the requisite amount of oxygen to give products in their stable forms.

23. (b) It is from the clear from the figure given.

24. (d) It is from the clear from the figure given.

DPP 5.4

Subjective Type

1. We are given (i) $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$, $\Delta H^\circ = -372.0$ kcal

(ii) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$, $\Delta H^\circ = -530.0$ kcal

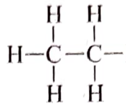
(iii) $C(s) \rightarrow C(g)$, $\Delta H^\circ = 172.0$ kcal

(iv) $H_2(g) \rightarrow 2H(g)$, $\Delta H^\circ = 104.0$ kcal

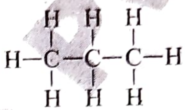
(v) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$, $\Delta H^\circ = -68.0$ kcal

(vi) $C(g) + O_2(g) \rightarrow CO_2(g)$, $\Delta H^\circ = -94.0$ kcal

Suppose the bond energy of C–C bond = x kcal $mole^{-1}$ and that of C–H bond = y kcal $mole^{-1}$. Then for



$C_2H_6(g)$, i.e., $H_3C{-}CH_3 \rightarrow 2C(g) + 6H(g)$, $\Delta H = x + 6y$ (vii)



and for $C_3H_8(g)$, i.e., $H_3C{-}CH_2{-}CH_3 \rightarrow 3C(g) + 8H(g)$,

$\Delta H = 2x + 8y$ (viii)

To get Eqn. (vii), operate Eqn. (i) + 2 × Eqn. (iii) + 3 × Eqn. (iv) –3 × Eqn. (v) –2 × Eqn. (vi).

This gives $\Delta H = 676$ kcal

To get Eqn. (viii), operate Eqn. (ii) + Eqn. (iii) + 4 × Eqn. (iv) –4 × Eqn. (v) –3 × Eqn. (vi).

This gives $\Delta H = 956$ kcal

Thus, $x + 6y = 676$

$2x + 8y = 956$

On solving these equations, we get $x = 82$, $y = 99$

Hence, C–C bond energy = **82 kcal mol^{-1}** and C–H bond energy = **99 kcal mol^{-1}**

2. $C_2H_5 - S - C_2H_5 + S(s) \longrightarrow C_2H_5 - S - S - C_2H_5$

$\Delta H_{reaction} = \Sigma\Delta H^\circ_{f(products)} - \Sigma\Delta H^\circ_{f(reactants)}$

$= (-202) - (-147) = -55$ kJ

$\Delta H_{reaction} = \Sigma(BE)_{reactants} - \Sigma(BE)_{products}$

-55 = Heat of sublimation or enthalpy of atomisation of sulphur $-BE(S-S)$

$-55 = 223 - BE(S-S)$

$BE(S-S) = 223 + 55 = 278$ kJ

(Common bonds of reactants and products are rejected.)

3. Given:

$F_2 \rightarrow 2F$; $\Delta H = 153.0$ kJ mol^{-1}

∴ $1/2\,F_2 \rightarrow F$; $\Delta H = 76.5$ kJ mol^{-1} (i)

and $Cl_2 \rightarrow 2Cl$; $\Delta H = 2424$ kJ mol^{-1}

∴ $1/2Cl_2 \rightarrow Cl$; $\Delta H = 1212$ kJ mol^{-1} (ii)

inverse of (i)

$F \rightarrow 1/2F_2$; $\Delta H = -76.5$ kJ mol^{-1}

inverse of (ii) $Cl \rightarrow 1/2Cl_2$; $\Delta H = -1212$ kJ mol^{-1}

On adding both the above equation energy

$F + Cl \rightarrow 1/2F_2 + 1/2Cl_2$;

$\Delta H = -1288.5$ kJ mol^{-1} (iii)

Also given

$1/2F_2 + 1/2Cl_2 \rightarrow FCl$; $\Delta H = 111.0$ kJ (iv)

(iii) + (iv)

$F + Cl \rightarrow FCl$; $\Delta H = -1177.5$ kJ mol^{-1}

Or $FCl \rightarrow F + Cl$; $\Delta H = +1177.5$ kJ mol^{-1}

4. Formation of N_2O

$N \equiv N\,(g) + 1/2O = O(g) \rightarrow N = N - O$

$$\Delta_f H^\circ cal = [\text{B.E. } (N \equiv N) + 1/2\text{B.E. } (O = O)]$$
$$- [\text{B.E.}(N = N) + \text{B.E}(N = O)]$$
$$= [946 + 1/2\ (498)] - [418 + 607]\ \text{kJ mol}^{-1}$$
$$= 170\ \text{kJ mol}^{-1}$$

$$\text{Resonance energy} = \Delta_f H^\circ(\text{obs}) - \Delta_f H^\circ(\text{cal})$$
$$= 82 - 170$$
$$= -88\ \text{kJ mol}^{-1}$$

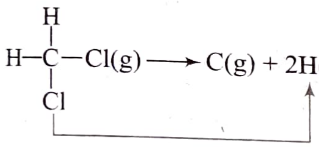
Single Correct Answer Type

5. (a) We have

$$\begin{tikzcd}
H_2(g) + \frac{1}{2}\ O_2(g) \arrow[r, "\Delta H"] \arrow[d, "\varepsilon_{H-H}\quad \frac{1}{2}\varepsilon_{O-O}"] & H_2O(g) \\
2H\ (g) + O(g) \arrow[ru, "-2\ \varepsilon_{O-H}"'] &
\end{tikzcd}$$

$$\text{Hence, } \varepsilon_{H-H} + \frac{1}{2}\varepsilon_{O=O} - 2\varepsilon_{O-H} = (433 + \frac{1}{2} \times 492)\ \text{kJ mol}^{-}$$
$$-2\varepsilon_{O-H} = -249\ \text{kJ mol}^{-1}$$
$$\varepsilon_{O-H} = \frac{1}{2}[(433 + \frac{1}{2} \times 492) + 249]\ \text{kJ mol}^{-1} = 464\ \text{kJ mol}^{-1}$$

6. (a)



$$H{-}\underset{Cl}{\overset{H}{C}}{-}Cl(g) \longrightarrow C(g) + 2H(g) + 2Cl$$

$$\Delta H_r = 2\varepsilon_{C\text{-}H} + 2\varepsilon_{C\text{-}Cl} = 2 \times 414 + 2 \times 330$$
$$= 828 + 660 = 1488\ \text{kJ/mol.}$$

7. (c)

(1) $H_2O(l) \rightarrow H_2O(g)$; $\Delta H = 40.6$ kJ mole

(2) $2H(g) \rightarrow H_2(g)$; $\Delta H = -435.0$ kJ mole

(3) $2O(g) \rightarrow O_2(g)$; $\Delta H = -489.6$ kJ mole

(4)
$$\begin{tikzcd}
2H_2(g) \arrow[d] & + & O_2(g) \arrow[d] \arrow[r] & H_2O(l) & \Delta H = -571.6\ \text{kJ/mole} \\
4H(g) & + & 2O(g) \arrow[ru] & &
\end{tikzcd}$$

(1) **Calculation of $\Delta H_f^o\ (H_2O, l)$**

$2H_2(g) + O_2(g) \rightarrow 2H_2O\ (l)$; $\Delta H = -571.6$ kJ/mole

$$\Delta H_r^o = 2\Delta H_f^o\ \{H_2O, (l)\} - 2\underset{\text{Zero}}{\underset{\downarrow}{\Delta H_f^o}}\ \{H_2, (g)\} - \underset{\text{Zero}}{\underset{\downarrow}{\Delta H_f^o}}\ \{O_2, (g)\}$$

$$-571.6 = 2\Delta H_f^o\ \{H_2O, (l)\}, \text{ so } \Delta H_f^o\ \{H_2O, (l)\} = -285.8$$

(2) **Calculation of $\Delta H_f^o\ \{H_2O, (g)\}$**

$(H_2O, l) \rightarrow \{H_2O(g)\}$; $\Delta H = 40.6$

$$\Delta H_r = \Delta H_f^o\ \{H_2O, (g)\} - \Delta H^o\ \{H_2O, (l)\}$$
$$\Delta H_f^o\ \{H_2O, (g)\} = \Delta H_f^o\ \{H_2O, (l)\} + \Delta H_r$$
$$= -285.8 + 40 = -245.8$$

(3)
$$\begin{tikzcd}
H_2(g) \arrow[d] & + & \frac{1}{2}O_2(g) \arrow[d] \arrow[r] & H_2O(g); & \Delta H = -245.8 \\
2H(g) & + & O(g) \arrow[ru] & &
\end{tikzcd}$$

$$\Delta H_r = \varepsilon_{H-H} + \frac{1}{2}\varepsilon_{O-O} - 2\varepsilon_{O-H}$$

$$\Rightarrow \quad -245.8 = +435 + \frac{1}{2}(489.6) - 2 \times \varepsilon_{O-H}$$
$$2\varepsilon_{O-H} = 435 + 244.8 + 245.8 \quad \Rightarrow \quad 2\varepsilon_{O-H} = 925.6$$
$$\varepsilon_{O-H} = 462.8$$

8. (c) $CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$; $\quad \Delta H = X_1$

So, Hydrogenation energy of benzene should be $3x_1$.

ΔH calculated $= 3x_1$

So, Resonance energy $= [3x_1 - x_2]$

9. (a) In polymerisation of ethylene, double bond of ethylene is broken and two single bonds are formed.

$CH_2 = CH_2 \rightarrow (-CH_2 - CH_2 -)$

$\Delta H_{poly} = E_{C=C} - 2\ E_{C-C} = -72 \Rightarrow E_{C=C} - 2E_{C-C} = -72$ (1)

$6C(s) + 3H_2(g) \rightarrow C_6H_6\ (l)$; $\quad \Delta H = 49$ kJ/mole

$\Delta_{resonance} = \Delta H_{exp} - \Delta H_{cal}$

$\Delta H_{cal} = 49 - (-\Delta H_{resonance}) = 49 - (-152) = 201$

(1) $6C(s) + 3H_2(g) \rightarrow C_6H_6(l)$; $\Delta H_{cal} = 201$

(2) $C_6H_6(l) \rightarrow C_6H_6(g)$; $\Delta H = 144$

Adding (1) and (2)

$$\begin{tikzcd}
6C(s) \arrow[d] + 3H_2(g) \arrow[d] \arrow[r] & C_6H_6(g);\ \Delta H = 345 \\
6C(g) + 6H(g) \arrow[ru] &
\end{tikzcd}$$

$\Delta H = 6 \times 715 + 3 \times 436 - 6E_{C-H} - 3E_{C=C} - 3E_{C-C}$

$345 = 4290 + 1308 - 6 \times 415 - 3E_{C=C} - E_{C-C}$

$3E_{C=C} + 3E_{C-C} = 2763$; So $E_{C=C} + E_{C-C} = 921$

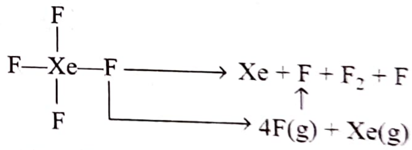
$E_{C=C} + E_{C-C} = 921$ (i)

$E_{C=C} - 2E_{C-C} = -72$ (ii)

On solving equations (i) and (ii) , $3E_{C-C} = 993$

$E_{C-C} = 331$ kJ/mole, $\quad$ So, $\quad E_{C=C} = 590$ kJ/mole

10. (c)



$$F{-}\underset{F}{\overset{F}{Xe}}{-}F \longrightarrow Xe + F + F_2 + F$$
$$\uparrow$$
$$\longrightarrow 4F(g) + Xe(g)$$

$$\Delta H = 4E_{Xe-F} + \Delta H_{ioni}\ [Xe \rightarrow Xe^+] - \Delta E_{F-F} - \Delta H_{eg}[F \rightarrow F^-]$$
$$= 4 \times 34 + 279 - 85 - 38 = 136 + 279 - 123 = 415 - 213$$
$$= 292\ \text{kcal/mole.}$$

Multiple Correct Answers Type

11. (a, b, c)

$\frac{1}{2}H_2 \rightarrow H$; $\Delta H^\circ = 218$ kJ. Let e_{C-C} be a and e_{C-H} be b kJ.

$\therefore \quad e_{H-H} = 436$ kJ

$2C + 3H_2 \rightarrow C_2H_6$; $\Delta_f H^\circ$

Also, $\Delta_f H^\circ\ C_2H_6 = -[e_{C-C} + 6e_{C-H}] + [2C_{s\rightarrow g} + 3e_{H-H}]$

$-85 = -[e_{C-C} + 6b] + [2 \times 718 + 3 \times 436]$ or $a + 6b = 2829$

$3C + 4H_2 \rightarrow C_3H_8 = -[2e_{C-C} + 8e_{C-H}] + [3C_{s\rightarrow g} + 4e_{H-H}]$

$-104 = -[2a + 8b] + [3 \times 718 + 4 \times 436]$ or $2a + 8b = 4002$

$a = 345$ kJ, $\quad b = 414$ kJ

12. (a, b, d)

$D_{C-C} + 6D_{C-H} = 620$ kJ

$2D_{C-C} + 8D_{C-H} = 880$ kJ

$\therefore \quad 2D_{C-C} + 12D_{C-H} = 1240$

$2D_{C-C} + 8D_{C-H} = 880$

$\therefore \quad 4D_{C-H} = 360$

$D_{C-H} = 90$ kJ/mol

$\therefore \quad D_{C-C} = 620 - 6 \times 90 = 620 - 540 = 80$ kJ/mol

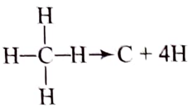
Matching Column Type

13. (A→a), (B→b), (C→c), (D→d)

(a) $H-H \rightarrow 2H$

$\therefore \Delta H = \Delta_f H$ of $H \times 2$

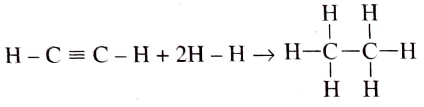
(b)



$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \rightarrow C + 4H$$

$\therefore \Delta H =$ Average bond energy × 4

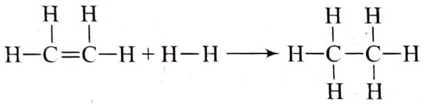
(c)



$$H-C \equiv C-H + 2H-H \rightarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

$\therefore \Delta H = e_{C\equiv C} - 4e_{C-H} + 2e_{C-C}$

(d)



$$H-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-H + H-H \longrightarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

$\therefore \Delta H = -e_{C=C} - e_{H-H} + e_{C-H} + e_{C-C}$

Integer Type

14.

$\frac{1}{2}A-A + \frac{1}{2}B-B \rightarrow AB \qquad \Delta H = -100$ kJ/mole

$\frac{1}{2}x + \frac{1}{2}(0.5x) - x = -100 \quad \Rightarrow \quad \frac{x}{2} + 0.25x - x = -100$

$\Rightarrow \quad -0.25x = -100 \qquad \Rightarrow \quad x = 400$ kJ/mole

Bond enthalpy = 400 kJ/mol

DPP 5.5

Subjective Type

1. $\Delta_r G^o = \Delta_r H^o - T\Delta_r S^o = 80000 \text{ J} - 400 \times 120 \text{ J} = 32000$ J

Now $\Delta_r G^o = -2.303$ RT log K

$\therefore \quad 32000 = -2.303 \times 8.314 \times 400 \times \log K$ or $\log K = -4.1782$

$= \bar{5}.8218$

$\therefore \quad K = \text{Antilog } \bar{5}.8218 = 6.634 \times 10^{-5}$

2. $\Delta_r H^o = (-1130.9) + (-241.8) + (-393.5) - 2 \times (-947.7)$

$= 129.2$ kJ mol^{-1}

$\Delta_r S^o = (136.0 + 188.8 + 213.7) - 2(102.1) = 334.3$ J K^{-1} mol^{-1}

$\Delta_r G^o = \Delta_r H^o - T\Delta_r S^o$.

At equilibrium, $\Delta G^o = 0$, $T = \frac{\Delta_r H^o}{\Delta_r S^o} = \frac{129200}{334.3} = 386.5$ K

Thus, above 386.5 K, $\Delta_r G^o$ will be negative and the reaction will be spontaneous.

3. $\Delta G^\circ = 2\Delta G^o_{ZnO} + 2\Delta G^o_{SO_2} - 2\Delta G^o_{ZnS}$

$= [-616 - 408] - [-293]$

$= -1024 + 293 = -731$ J

4. Given $K = 2.0 \times 10^{-7}$

$T = 300$ K.

$\Delta H^\circ = 28.4$ kJ mol^{-1}

$\Delta G^\circ = -2.303$ RT log K

$= -2.303 \times 8.314 \times 10^{-3} \times 300 \times \log(2 \times 10^7)$

$= -5.744 (\log 2 - 7)$

$= -5.744 (0.3010 - 7)$

$= 38.48$ kJ

From $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Rightarrow \quad \Delta S^\circ = \Delta H^\circ - \Delta G^\circ$

$$\Delta S^\circ = \frac{\Delta H^\circ - T\Delta S^\circ}{T}$$

$$= \frac{28.4 - 38.48}{30}$$

$= 0.0336$ kJ mol^{-1}

or $\quad \Delta S = -33.6$ J mol^{-1} K^{-1}

5. $\Delta S_{sys} = nR \ln \frac{V_2}{V_1} + nC_v \ln \frac{T_2}{T_1}$

$\Delta S_{system} = nR \ln \frac{V_2}{V_1} = 2 \times 8.314 \ln 2.5 = 15.32$ J

$\Delta S_{surr} = -\frac{4.17 \times 10^3}{300} = -13.9$ J

$\Delta S_{univ} = 1.42$ J

6. Process is adiabatic and irreversible.

$\therefore \quad \Delta q = 0 \quad$ and $\quad \Delta E = \Delta W$

$\therefore \quad nC_v(T_2 - T_1) = -P_{ext}(V_2 - V_1)$

$n = 1;\ C_v = \frac{3}{2}R;\ T_1 = 300 \text{ K};\ P_{ext} = 0.3$ atm

$V_1 = \frac{nRT_1}{P_1} = \frac{1 \times 0.082 \times 300}{1}$

$V_2 = 2 \times 0.082 \times 300$

$\therefore \quad 1 \times \frac{3}{2} \times 0.082 \times (T_2 - 300)$

$= -0.3 \times 0.082 \times 300$

or $\quad \frac{3}{2}T_2 - 450 = -90$

or $\quad \frac{3}{2}T_2 = 360 \quad$ or $\quad T_2 = 240$ K

$\therefore \quad \Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$

or $\quad \Delta S = \frac{3}{2} \times R \times 2.303 \log \frac{240}{300} + R \times 2.303 \times \log 2$

or $\quad \Delta S = \frac{3}{2} \times R \times 2.303 \log \frac{4}{5} + R \times 2.303 \times \log 2$

or $\quad \Delta S = 2.303 \times R \left[\frac{3}{2}(2 \log 2 - \log 5) + \log 2\right]$

or $\quad \Delta S = 2.303 \times R \left[4 \log 2 - \frac{3}{2} \log 5\right]$

or $\Delta S = 2.303 \times R\left[4\log 2 - \frac{3}{2}\log 5\right]$

or $\Delta S = 2.303 \times R[1.2 - 1.05]$

or $\Delta S = 0.345 \times 8.314 = 2.872 \text{ J K}^{-1} \text{ mol}^{-1}$.

Single Correct Answer Type

7. (b) ($\Delta S = \Delta H/T = 40.63 \times 10^3 \text{ J mol}^{-1}/373 \text{ K} = 108.9 \text{ J K}^{-1} \text{ mol}^{-1}$

8. (a) ($K_p = p_B/p_A = 1/4$. Since $\Delta G^\circ = -RT \ln K_p^\circ$, we will have $\Delta G^\circ = RT \ln 4$

9. (b) ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = [-54.07 \times 10^3 - (298)(10)] \text{ J mol}^{-1}$

$$= -57050 \text{ J mol}^{-1}$$

$$K^\circ = \frac{-\Delta G^\circ}{2.303RT} = \frac{57050 \text{ J mol}^{-1}}{5705 \text{ J mol}^{-1}} = 10$$

10. (b)

$$2O_3 \xrightarrow{300\text{ K}} 3O_2;\ \Delta H = -68 \text{ kcal};\ \Delta S = +\text{ve}.$$

11. (c)

Δn_g is +ve

12. (c)

$$\Delta S = nC_{p,m} \ln \frac{T_2}{T_1} = 2 \times \frac{5}{2} R \ln \frac{600}{300} = 5R \ln 2$$

13. (c) In the initial state, $p_{AB} = 0$

$$\therefore \Delta G = 19.147 + RT \ln \frac{0}{1 \times 5} = 19.147 + RT \ln e^{-\infty}$$

$$= -\infty$$

Multiple Correct Answers Type

14. (a, c)

(a) $\Delta S_{x\to z} = \Delta S_{x\to y} + \Delta S_{y\to z}$

(because entropy is a state function and hence additive)

(b) $w_{x\to z} \neq w_{x\to y} + w_{y\to z}$

(c) $w_{x\to y\to z} = w_{x\to y}$ (because $w_{y\to z} = 0$ as it is an isochoric process)

(d) $\Delta S_{x\to y\to z} \neq \Delta S_{x\to y}$ but $= \Delta S_{x\to y} + \Delta S_{y\to z}$

Thus, only (a) and (c) are correct.

15. (b, c, d)

$\Delta G^\circ = 0$ at equilibrium under standard state. Also, at eq. $\Delta G = 0$

$\therefore \quad \Delta H^\circ - T\Delta S^\circ = 0$

Also, $\Delta G^\circ = 2.303\, RT \ln K$

$\therefore \quad K = 1$

16. (b, c, d)

$H_2O(s)$ has more ordered arrangement. Also,

$$\Delta S_2^o = S^o_{H_2O(v)} - S^o_{H_2O(l)}$$

$$\Delta S_0^1 = S^o_{H_2O(l)} - S^o_{H_2O(s)}$$

$\therefore S^o_{H_2O(v)}$ is maximum and this $\Delta S_2^o >>> \Delta S_1^o$.

17. (a, c, d)

18. (b, d)

Vaporization of camphor entropy increase.

⇔ gaseous phase

$H_2 \to H + H$

Atomization ⇒ Dihydrogen is stable but atomic hydrogen is very reactive. Thus increase in entropy occurs.

19. (b, c, d)

Increase in no. of moles increases entropy.

20. (a, c)

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S$$

Matching Column Type

21. **(A→1, 2, 3), (B→1, 4), (C→1, 2, 3), D→(1, 3, 4)**

$H_2O(l) \rightleftharpoons H_2O(g) : \Delta G < 0, \Delta H > 0, \Delta S > 0$

$C(s) + O_2(g) \rightarrow CO_2(g) : \Delta G < 0, \Delta H < 0$

$H_2O(s) \rightleftharpoons H_2O(l) : \Delta G < 0, \Delta H > 0, \Delta S > 0$

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) : \Delta G < 0, \Delta S > 0, \Delta H < 0$

Integer Type

22. (5) $\Delta_{sus}S = \Delta_{sub}H/T = 1365/273 = 5$

23. (1) Let the resultant temperature of mixture is T K.

then $\frac{64}{32} \times 81.6 \times (333 - T) = \frac{128}{32} \times 81.6 \times (T - 293)$

$\Rightarrow \quad T = 306.3 \text{ K}$

ΔS due to cooling of added $CH_3OH = nC_p \ln \frac{T_2}{T_1}$

$= 2 \times 81.6 \times 2.303 \times \log \frac{306.3}{333}$

$= -13.51 \text{ J/K}$

ΔS due to heat ions of CH_3OH in the vessel

$= 4 \times 81.6 \times 2.303 \times \log \frac{306.3}{393}$

$= +14.51 \text{ J/K}$

$\Rightarrow \quad \Delta S_{total} = 14.51 - 13.53 \text{ J/K} = 0.98 \text{ J/K}$

$\sim 1 \text{ JK}^{-1}$

Comprehension Type

24. (b) $\Delta S = nR \ln \frac{V_2}{V_1}$ (For/mole)

$= 8.31 \times 2.30\,3 \times \log_{10}3$

$\simeq 9.1 \text{ J/K mol}^1$

25. (b) Again $\Delta S = nR \ln \frac{V_2}{V_1}$

$\Delta S = 5 \times 8.31 \times 2.303 \times 5$

$= 45.66 \text{ J/K}$

26. (d) $\Delta Q = P\Delta V = 1 \times 10^5 \times (10 - 30) = -2000 \text{ J}$

$\therefore \Delta S = \frac{-2000}{273 + 15} = -6.94 \text{ J/K}$

27. (c) $G = H - TS$

or $\quad G = U + PV - TS$

Differentiating above equation, we get

$$dG = dU + PdV + VdP - TdS - SdT$$

or $\quad dG = dq + VdP - SdT - dq = VdP - SdT$

or $dG = VdP - SdT$ (I)

Since G is a state function and $G = \phi(P, T)$, therefore by applying Euler's rule, we get

$$G = \phi(P, T)$$

or $dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial P}\right)_P dT$ (II)

By comparing the coefficients of equation (I) and (II) we can write, $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S$

28. (a) $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S$

Since G is a state function, therefore by applying Euler's reciprocity relation,

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

29. (d) $A = U - TS$

or $dA = dU - TdS - SdT$

or $dA = dU - dq - SdT = dU - dU - PdV - SdT$

or $dA = -PdV - SdT$

$\therefore$ $\left(\frac{\partial A}{\partial T}\right)_V = -S$ and $\left(\frac{\partial A}{\partial V}\right)_T = -P$

Since A is a state function, therefore by applying Euler's reciprocity relation,

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

30. (d) $\Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$

At the definite temperature

$\Delta S = -nR \ln P_2/P_1$

or $\Delta S = -nR \ln P$ [$\because P_1 = 1$]

31. (b) $\Delta S_{sys} = C_v \ln \frac{T_2}{T_1} + R\ln \frac{V_2}{V_1} = R\ln 3$

Since $\Delta q = 0$, hence, $\Delta S_{surr} = 0$

$\therefore$ $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = R\ln 3$

DPP 5.6

Subjective Type

1. Rise in temperature = 300.78 – 294.05 = 6.73 K

Heat transferred to the calorimeter = Heat capacity of the calorimeter × Rise in temp.

$= (8.93 \text{ kJ K}^{-1})(6.73 \text{ K}) = 60.1 \text{ kJ}$

Molar mass of $C_8H_{18} = 8 \times 12 + 18 = 114 \text{ g mol}^{-1}$

$\therefore$ Enthalpy of combustion $= \frac{60.1}{1.250} \times 114 \text{ kJ mol}^{-1}$

$= 5481.1 \text{ kJ mol}^{-1}$

2. Total ΔH = (1 mol water at 10°C → 1 mol of water at 0°C) + (1 mol water at 0°C → 1 mol ice at 0°C) + (1mol ice at 0°C → 1 mol ice at –10°C)

$= C_p[H_2O(l) \times \Delta T + \Delta H_{freezing} + C_p[H_2O(s)] \times \Delta T$ $(\Delta T = T_2 - T_1)$

$= (75.3 \text{ J K}^{-1} \text{ mol}^{-1})(0 - 10) \text{ K} + (-6.03 \text{ kJ mol}^{-1}) + (36.8 \text{ J K}^{-1} \text{ mol}^{-1})(-10 \text{ K})$

$(\Delta_{freezing} = -\Delta H_{fusion})$

$= -753 \text{ J mol}^{-1} - 6.03 \text{ kJ mol}^{-1} - 368 \text{ J mol}^{-1}$

$= -0.753 \text{ kJ mol}^{-1} - 6.03 \text{ kJ mol}^{-1} - 0.368 \text{ kJ mol}^{-1}$

$= -7.151 \text{ kJ mol}^{-1}$

Note: Directly also, as in each step, heat is evolved, each step will have a negative sign with ΔH.

3. For monoatomic ideal gas, $C_v = \frac{3}{2}R$, $C_p = \frac{5}{2}R$

But $C_p = \frac{\Delta H}{\Delta T}$

$\therefore$ $\Delta H = C_p \Delta T \cdot \text{mol}^{-1}$ (or $nC_p \Delta T$ for n moles)

$= \frac{5}{2} \times 1.987 \times 25 = 124.2$ cal

Work done, $w = -P\Delta V = -\Delta(V_2 - V_1) = (PV_2 - PV_1)$

$= (-nRT_2 - nRT_1) = -nR(T_2 - T_1)$

$= -1 \times 1.987(323 - 298)$ cal $= -49.7$ cal

$\Delta U = q + w = 124.2 = 49.7$ cal $= 74.5$ cal

4. Heat of combustion of fuel

$$\Delta E = \frac{(w+m)s \times (t_2 - t_1) \cdot M}{w_1} \text{ kcal}$$

W = water equivalent (mole given)

M = molecule wt. of fuel = 28

m = mass of water = 1 g

W_1 = wt . of fuel taken

T_2 = final temp = 67.3°C

T_1 = initial temp and 1 cal g^{-1} 0°C^{-1} = 25°C

$$\Delta E = -\frac{(0+1) \times 1 \times (67.3 - 25) \times 28}{3.5}$$

$= -338.4$ kcal

Single Correct Answer Type

5. (a) No doubt more heat will be liberated in I reaction which will be used to heat mixture (400 mL). In II heat liberated will be ¼ of I which will be used to heat mixture (1/4 of I, i.e., 100 mL).

6. (b) $C_p = \left(\frac{\partial H}{\partial T}\right)_P$; At equilibrium T is constant, i.e., molar heat capacity at equilibrium is infinity.

7. (c) The conservation of heat gives $m_i C_i (20 \text{ K}) + m_1' \Delta_{fus}H - m_w C_w (20 \text{ K}) = 0$

$(4 \text{ kg})(2.092 \text{ kJ J}^{-1} \text{ kg}^{-1})(20 \text{ K}) + m_1' (334.7 \text{ kJ kg}^{-1}) - (10 \text{ kg})(4.184 \text{ kJ K}^{-1} \text{ kg}^{-1})(20 \text{ K}) = 0$

This gives

$$m_1' = \left[\frac{(10)(4.184)(20) - (4)(2.092)(20)}{334.7}\right] \text{kg}$$

$$= \left(\frac{936.8 - 167.36}{334.7}\right) \text{kg} = \left(\frac{669.44}{334.7}\right) \text{kg} = 2.0 \text{ kg}$$

Hence, mass of water in the container is $m' = (10\text{ kg}) + (2\text{ kg})$

$= 12\text{ kg}.$

8. (b) Since ice-water ratio is maintained as 1:1. So, $\Delta T = 0$

9. (a) Let final common temperature is T_f.

Heat gained by Zinc piece = Heat lost by water

$0.4(T_f - 20) \times 65.38 = 4.2(100 - T_f) \times 180 \Rightarrow T_f = 97.3°C$

10. (c) $\Delta H° = -92.2$

$$\Delta C_P = 2C_P(NH_3, g) - C_P(N_2, g) = 3C_P(H_2)$$
$$= 2 \times 35.1 - 29.1 - 3 \times 28.8$$
$$= 70.2 - 29.1 - 86.4$$
$$= -45.3\text{ J/K}$$
$$\Delta H^o_{100°C} = -92.2 - 1.3975 = -95.6\text{ kJ/mole}$$

Then, reaction at 100°C as compared to that at 25°C will be more exothermic.

11. (a) $\Delta G^o_{200} = \Delta H^o_{200} - T\,\Delta S^o_{200}$

$\Delta H^o_{200} = 20 - 4 = 16\text{ kJ/mol}$

$\Delta H^o_{T_2} = \Delta H^o_{T_1} + \Delta C_p[T_2 - T_1]$

$$\Delta H^o_{400} = \Delta H^o_{200} + \frac{20 + 200}{1000}\text{kJ/mol} = 16 + 4 = 20\text{ kJ/mol.}$$

12. (d) $\Delta C_P = C_P(HCl) - \frac{1}{2}C_P(H_2) - \frac{1}{2}C_P(Cl_2)$

$$= 6.81 - \frac{1}{2} \times 6.82 - \frac{1}{2} \times 7.71$$
$$= 6.381 - 3.41 - 3.855 = -0.45$$
$$\Delta H_{348} = \Delta H_{298} + (\Delta C_p)(\Delta T) = -22060 + (-0.45) \times 50$$
$$= -22082.5\text{ cal}$$

Multiple Correct Answers Type

13. (a, b, d, e)

(a) follows from $\Delta H = \Delta E + \Delta nRT$. (b) is well known relationship. (c) is wrong because $\Delta U = q + w$. (d) follows from $-\Delta G° = RT\ln K$. (e) represents Kirchoff equation.

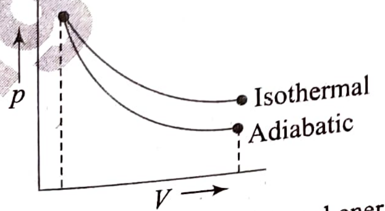
14. (a, c)

$$\text{We have } C_{p,m}\text{ (mixture)} = \frac{1}{2}(C_{p1} + C_{p2}) = \frac{1}{2}\left(\frac{5}{2}R + \frac{7}{2}R\right) = 3R$$

$$C_{V,m}\text{ (mixture)} = \frac{1}{2}(C_{V1} + C_{V2}) = \frac{1}{2}\left(\frac{3}{2}R + \frac{5}{2}R\right) = 2R$$

$\gamma = C_{p,m}/C_{V,m} = 3R/2R = 3/2$

The choice (b) is incorrect as may be seen from the areas under the isothermal and adiabatic curves shown in Figure.



The choice (c) is correct as the internal energy of an ideal gas depends only on temperature.

The choice (d) is also incorrect as shown in the following.

Heat used in increasing internal energy = $C_V\,\Delta T$

Heat absorbed at constant pressure = $C_p\,\Delta T$

Fraction of heat used in increasing internal energy is

$$\phi = \frac{C_V\Delta T}{C_p\Delta T} = \frac{C_V}{C_p}$$

For one mole of the gas, $\phi = \frac{C_{V,m}}{C_{p,m}} = \frac{(5/2)R}{(7/2)R} = \frac{5}{7}$

15. (a, b, c, d)

$$\frac{C_p}{C_v} = 1.4 = \gamma$$

$$C_p - C_v = R$$

$\therefore \gamma C_v - C_v = R \quad \therefore C_v = \frac{R}{\gamma - 1}$ and similarly $C_p - \frac{C_{-p}}{\gamma} = R$

$\therefore \quad C_v\frac{2}{0.4} = 5\text{ cal} \qquad \therefore C_p = \frac{\gamma \cdot R}{(\gamma - 1)}$

Also, $C_v = \frac{2}{0.4 \times 32} = 0.156\text{ cal}$

Matching Column Type

16. (a→p, q), (b→p, q), (c→s), (d→r)

O_2, N_2 → For diatomic gases

$$C_\upsilon = \frac{5}{2}R \;;\; C_P = \frac{7}{2}R$$

$$\gamma = \frac{C_P}{C_\upsilon} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.4$$

CO_2, CH_4 → For tri and poly atomic gases: $\gamma = \frac{4R}{3R} = 1.33$

1 mol O_2 + 2mol O_3 →

$$C_P = \frac{n_1C_{P1} + n_2C_{P2}}{n_1 + n_2} = \frac{1 \times \frac{7}{2}R + 2 \times 4R}{1 + 2} = \frac{23}{6}R$$

Integer Type

17. (9) Enthalpy of combustion of 3.5 g of the gas

$= (2.5\text{ kJ K}^{-1})(0.45\text{ K}) = 1.125\text{ kJ}$

As molar mass of the gas is 28, enthalpy of combustion per

mole $= \frac{1.125}{3.5} \times 28\text{ kJ} \approx 9\text{ kJ}$

18. (2) $q = m.C_v\Delta \;\Rightarrow\; q = \frac{100}{18} \times 75\,\Delta T$

$$\Delta T = \frac{q}{mC_v}$$

$$\Delta T = \frac{850}{100} \times \frac{18}{75} = 2.04\text{ K}$$

Comprehension Type

19. (b) From the first law of thermodynamics, we have

$\Delta U_1 = q_1 + w_1 = 5960\text{ J} - 2200\text{ J} = 3760\text{ J};$

$\Delta U_2 = q_2 + w_2 = -5585\text{ J} + 825\text{ J} = -4760\text{ J}$

$\Delta U_3 = q_3 + w_3 = -2980\text{ J} + 1100\text{ J} = -1880\text{ J}$;

$\Delta U_4 = 3645\text{ J} + w_4$

Since the process is cyclic, the net ΔU (= $\Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4$) will be equal to zero.

Hence, $3760\text{ J} - 4760\text{ J} - 1880\text{ J} + (3645\text{ J} + w_4) = 0$

This gives $w_4 = -765\text{ J}$

20. (c) $\Delta U_{net} = 0$, See part (i)

21. (a) Steps 1 and 2 taken together will accompany with a net decrease in the internal energy of the gas.

22. (a) Molar enthalpy of vaporization of H_2O at 0°C is $\Delta H = \Delta C_p . \Delta T$

$H_2 - H_1 = (C_{p2} - C_{p1})(T_2 - T_1)$

From Q – for vaporization

$H_2O(l) \rightarrow H_2O(g)$

$\Delta H = H(g) - H(l)$

100 0

$$40.66 - H = \frac{(30.5 - 75.5)}{1000} \times 100$$

$$\Rightarrow 40.66 - H = \frac{4.5}{10}$$

$\mu = 45.16$ kJ/mol

23. (c) $\Delta H = H_{solid} - H_{liquid} = \Delta C_p\, \Delta T$

$\Rightarrow H_{solid} - H_{liquid} = \Delta C_p\, \Delta T$

$$\Rightarrow 6 - H_{liquid} = \frac{(35.5 - 75.5)}{1000}$$

$$\Rightarrow 6 - H_{liquid} = \frac{40}{100}$$

$\Rightarrow -H_{liquid} = -6 - 4$

$-H_{liquid} = -10$ kJ/mole

$\boxed{H_{liquid} = 10\text{ kJ/mole}}$

24. (d) Molar enthalpy of sublimation of H_2O at 100°C in kJ/mole.

CHAPTER 6

DPP 6.1

Subjective Type

1. (1) A system is said to be homogeneous if phase (P) = 1. A system with P ≥ 2 is heterogeneous.

(2) To determine phase, follow the rules given below.

System	Phase	Explanation
S + S	= 2	No. of solid in mixture give number of P, i.e., P = 2
S + L	= 1	Soluble systems lead to P = 1
S + L	= 2	Soluble systems lead to P = 2
L + L	= 2	Immiscible liquids lead to P = 2
L + L	= 1	Miscible liquids lead to P = 1
G + G	= 1	All gases in a mixture give P = 1

Given Systems	a	b	c	d	e	f	g
No. of phases	2	2	2	2	1	2	3

∴ Homogeneous system is : **e**

Heterogeneous system are: **a, b, c, d, f, g**

2. **Note:** 1. Write K_P for heterogeneous system if gaseous phase is present.

2. Write K_C for homogeneous solution phase.

3. Write K_P or K_C for homogeneous gaseous phase.

(a) $K_P = [P'_{O_2}]^{3/2}$

(b) $K_p = [P'_{H_2O}]/P'_{H_2} = \dfrac{nH_2O}{nH_2} \times [P/\Sigma N]^0$

(c) $K_P = [P'CO_2]^2/[P'_{O_2}]^5 = \dfrac{[nCO_2]^2}{[nO_2]^5} \cdot \left[\dfrac{P}{\Sigma N}\right]^{-3}$

(d) $K_P = \dfrac{[P'_{HI}]^2}{P'_{H_2} \times P'_{I_2}}$ or $K_C = \dfrac{[HI]^2}{[H_2][I_2]}$

(e) $K_P = \dfrac{[P'_{NH_3}]^2}{[P'_{N_2}][P'_{H_2}]^3}$ or $K_C = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

(f) $K_C = \dfrac{[CH_3COOCH_3][H_2O]}{[CH_3COOH][CH_3OH]}$

3. According to the reaction stoichiometry, $I_2(g) \rightleftharpoons 2I(g)$

Then $P_{I(g)} = P_{total} \times$ Fraction of I atoms $= 10^5 \text{ Pa} \times 0.4$

and $P_{I_2(g)} = P_{total} \times$ Fraction of I_2 molecules $= 10^5 \text{ Pa} \times 0.6$

$$K_p = \frac{(P_{I(g)})^2}{P_{I_2(g)}} = \frac{(0.4 \times 10^5 \text{ Pa})^2}{0.6 \times 10^5 \text{ Pa}} = 2.67 \times 10^4 \text{ Pa}.$$

4. Since, there are only two gaseous species in the above equilibrium.

∴ $p_{CO_2} = p_{H_2O} = \dfrac{1}{2}$ total pressure $= \dfrac{1}{2} \times 1.04 = 0.52$ atm

$$K_p = p_{CO_2} \times p_{H_2O} = [0.52]^2 = 0.2704 \text{ atm}$$

Single Correct Answer Type

5. (b) In the reaction, $Fe^{3+} + SCN^- \rightleftharpoons \underset{\text{(Red)}}{FeSCN^{2+}}$

When oxalic acid is added it combines with Fe^{3+} ions, then equilibrium shifts towards backward direction and intensity of red colour decreases.

6. (d) Reaction: $2A + B \rightleftharpoons C + D$

$$K_P^o = \frac{n_C \times n_D}{n_A^2 \times n_B} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n_g}$$

$$\Delta n_g = 2 - 3 = -1$$

$$K_P^o = \frac{n_C \times n_D}{n_A \times n_B} \times \left(\frac{\Sigma n}{P}\right) \quad \text{(i)}$$

$$PV = \Sigma nRT$$

$$\frac{V}{RT} = \frac{\Sigma n}{P} \quad \text{(ii)}$$

From eqs. (i) and (ii),

$$K_p^o = \frac{n_C \times n_D}{n_A^2 \times n_B} \times \frac{V_P^o}{RT}$$

7. (b) Concentration of $[NO_2]$ will decrease with increase in concentration $[N_2O_4]$.

8. (a) With passage of time conc. of reactants decreases and products increases.

9. (c) In region (I), the concentration of reactants and products are constant, hence this region shows equilibrium.

10. (d) Acc. of Henry's law $K_P = \dfrac{a}{p} = \dfrac{2.21 \times 10^{-3}}{1}$

$= 2.21 \times 10^{-3}$ mol atm^{-1}

Now, O_2 required for survival $= 4 \times 10^{-3}$ g/litre

$= \dfrac{4 \times 10^{-3}}{32}$ mol litre^{-1}

Now, $2.21 \times 10^{-3} = \dfrac{4 \times 10^{-3}}{P \times 32}$

∴ P = 0.056 atm

11. (a) $\underset{a-x}{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{b+x}{B}$ $\quad k_c = \dfrac{k_1}{k_2} = \dfrac{b+x}{a-x}$

$x = \dfrac{k_1 a - k_2 b}{k_1 + k_2}$. Therefore, option (a) is correct.

12. (b) $LaCl_3(s) + H_2O(g) + \text{heat} \rightarrow LaClO(s) + 2HCl(g)$

$K_p = \dfrac{p_{HCl}^2}{p_{H_2O}} = \dfrac{p'^2_{HCl}}{2p_{H_2O}} \qquad p'_{HCl} = \sqrt{2}\, P_{HCl}.$

Multiple Correct Answers Type

13. (a, d)

At a particular temperature and atmospheric pressure, the solid and liquid phases of a pure substance can exist as solid $\rightleftharpoons$ liquid.

They exists at normal melting point or normal freezing point.

14. (a, b, d)

On spraying NaCl on ice, m.pt. of ice is lowered and melts earlier.

15. (a, b, c, d)

Heterogeneous have P > 1; two solids have two phases.

16. (a, b, c, d)

Distribution of gas occurs between gaseous and solution phase.

$$\begin{array}{lcl} \text{Gas} + H_2O & \rightleftharpoons & \text{Solution} \\ \text{Phase I} & & \text{Phase II} \end{array}$$

17. (b, d)

Given $K_C < 2$, therefore in case of B and C.

$$K_C = \frac{2 \times 4}{6} = \frac{4}{3}$$

and concentration of PCl_3 and Cl_2 together will decrease or increase as reaction can go in the forward or backward direction.

Matching Column Type

18. (a→q), (b→p, t), (c→r), (d→s)

Unit of K_p = (Unit of pressure) $^{\Delta n_g}$

Reaction	Δn_g	**Unit of K_p**
⇒ $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$	0	Unitless
⇒ $3O_2(g) \rightleftharpoons 2O_3(g)$	−1	atm^{-}, bar^{-1}
⇒ $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$	$-\frac{1}{2}$	bar$^{-1/2}$
⇒ $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$	−2	atm^{-2}

Comprehension Type

19. (a)

Among SO_2 and O_2 initial moles of SO_2 required should be greater.

20. (a) At equilibrium $r_f = r_b$

21. (b) At equilibrium when additional quantity of A is added, rate of forward reaction increases because of the concentration of the reacting molecules increases. The rate of forward reaction becomes faster than that of the backward reaction, so the system is out of the equilibrium. However, as the concentration of C and D increase, the rate of the reverse reaction increases, while the decrease in the concentrations of A and B causes the rate of the forward reaction to decrease. The rates of the two reactions become equal, and a second stage of equilibrium is reached, but equilibrium constant remain the same.

DPP 6.2

Subjective Type

1. According to integrated van't Hoff equation

$$\log\frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H°}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Putting $(K_p)_2/(K_p)_1 = 2$, $T = 25°C = 298$ K, $T_2 = 35°C = 308$ K, R = 8.314 JK^{-1} mol^{-1}, we get

$$\log 2 = \frac{\Delta H°}{2.303 \times 8.314\ \text{J K}^{-1}\text{mol}^{-1}} \times \frac{(308 - 298)\text{K}}{298\ \text{K}\ 308\ \text{K}}$$

or $\quad \Delta H° = 52898\ \text{J mol}^{-1} = 52.898\ \text{kJ mol}^{-1}$

2. $S + S^2 \rightleftharpoons S_2^{2-}; K_1 = 12$ (1)

$2S + S^{2-} \rightleftharpoons S_3^{2-}; K_2 = 132$ (2)

$S + S_2^{2-} \rightleftharpoons S_3^{2-}; K_3 = ?$

$$K_1 = \frac{(S_2^{2-})}{(S) \times (S^{2-})}$$

Equation (2 ÷ 1)

$$= \frac{K_2}{K_1} = \frac{(S_3^{2-})}{(S)^2 \times (S^{2-})} \times \frac{(S)(S^{2-})}{(S_2^{2-})}$$

$$K_3 = \frac{(S_3{}^{2-})}{(S) \times (S_2^{2-})} = \frac{K_2}{K_1} = \frac{(S_3^{2-})}{(S) \times (S_2^{2-})}$$

$$K_3 = \frac{(S_3^{2-})}{(S) \times (S_2^{2-})} = \frac{132}{12}$$

$$= 11$$

3. (a) This reaction will have appreciable concentration of the reactant i.e., of $Cl_2(g)$.

(b) This reaction will have appreciable concentration of the products i.e., of NOCl(g).

(c) This reaction will have nearly the same concentrations of reactants and products.

4. K_C for net reaction $= \dfrac{[NOBr]}{[Br_2]^{1/2}[O_2]^{1/2}[N_2]^{1/2}}$

Given reactions are, $2.4 \times 10^{30} = \dfrac{[N_2][O_2]}{[NO]^2}$ (1)

$$1.4 = \frac{[NOBr]}{[NO][Br]^{1/2}} \quad (2)$$

From direct observation one can conclude that net reaction can by obtained by subtracting eq. (1) × $\frac{1}{2}$ from eq. (2).

So, respective values of K_C will be now

$$\frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}} = \left(\frac{1}{2.4 \times 10^{30}}\right)^{1/2} \quad (3)$$

On multiplying eq. (3) and eq. (2)

$$\frac{[NOBr]}{[NO]\,[Br_2]^{1/2}} \times \frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}} = 1.4 \times \frac{1}{(2.4 \times 10^{30})^{1/2}}$$

or $\quad \dfrac{[NOBr]}{[Br_2]^{1/2}[O_2]^{1/2}[N_2]^{1/2}} = K_C = 9 \times 10^{-16}$

5. For given reaction, $K_p = (P_{H_2O})^2$

So $K_P\,(25°C) = (7 \times 10^{-3})^2\ atm^2 = 4.9 \times 10^{-5}\ atm^2$

Since ΔH° = 2750 cal, so using van't Hoff equation.

$$\log\frac{[K_p(127°C)]}{[K_P(25°C)]} = \frac{\Delta H°}{2.303 \times R}\left[\frac{400 - 298}{400 \times 298}\right]$$

$$\log\frac{[K_P(127°C)]}{[4.9 \times 10^{-5}]} = \frac{2750}{2.303 \times 2}\left[\frac{102}{119200}\right]$$

$$K_p(127°C) = 3.2426 \times 4.9 \times 10^{-5}$$

So, p_{H_2O} at 127°C $= \sqrt{K_P(127°C)} = 1.26 \times 10^{-2}$ atm

Single Correct Answer Type

6. (a) $\text{Slope} = -\dfrac{\Delta H°}{2.303R}$

$$\tan 45° = -\frac{\Delta H°}{2.303 \times 8.314}$$

$$\Delta H° = -2.303 \times 8.314 = -19.14\ J\ mol^{-1}$$

7. (d) At point 'A',

$Q = \tan 60° = 1.732$

$\therefore\ \ Q = K$

8. (a) For the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g);\ K = P_{CO_2}$

We know $\log_{10} K = \log_{10} A - \dfrac{\Delta H°}{2.303R} \times \dfrac{1}{T}$

$$\log_{10} P_{CO_2} = \log_{10} A - \frac{\Delta H°}{2.303R} \times \frac{1}{T}$$

The reaction is endothermic, therefore, $\log_{10} P_{CO_2}$ will linearly decrease with increase in the value of $\left(\dfrac{1}{T}\right)$.

9. (b) $K_p = P_{C_{10}H_8(g)} = 0.10$ mm

$$= \frac{0.10}{760}\text{atm} = 1.32 \times 10^{-4}\ \text{atm}$$

$C_{10}H_8(s) \rightleftharpoons C_{10}H_8(g),\ \Delta n = 1$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{K_p}{RT} = \frac{1.32 \times 10^{-4}}{0.0821 \times 300} = 5.36 \times 10^{-6}$$

10. (a) $N_2 + O_2 \rightarrow 2NO,\ K = 4 \times 10^{-4}$

For the reverse reaction,

$2NO \rightarrow N_2 + O_2,\ K = \dfrac{1}{4 \times 10^{-4}}$

On dividing by 2, $NO \rightarrow \dfrac{1}{2}N_2 + \dfrac{1}{2}O_2$

$$K = \sqrt{\frac{1}{4 \times 10^{-4}}} = \frac{1}{2 \times 10^{-2}} = 50$$

11. (c) For $2PQ \rightleftharpoons P_2 + Q_2,\ K_1 = \dfrac{[P_2][Q_2]}{[PQ]^2}$

For $PQ + \dfrac{1}{2}R_2 \rightleftharpoons PQR,\ K_2 = \dfrac{[PQR]}{[PQ][R_2]^{1/2}}$

For the required equilibrium,

$\dfrac{1}{2}P_2 + \dfrac{1}{2}Q_2 + \dfrac{1}{2}R_2 \rightleftharpoons PQR$

$$K = \frac{[PQR]}{[P_2]^{1/2}[Q_2]^{1/2}[R_2]^{1/2}} = \frac{K_2}{\sqrt{K_1}}$$

$$= \frac{5 \times 10^{-3}}{\sqrt{2.5 \times 10^5}} = \frac{5 \times 10^{-3}}{5 \times 10^2} = 10^{-5}$$

12. (a) The formation of SO_3 is exothermic and thus at high temperature backward reaction will proceed to give lower percentage yield.

13. (a) $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$

$K_p = 0.03;\quad T = 477°C = 700\ K$

$K_p = K_C(RT)^1$

$$K_C = \frac{K_P}{RT} = \left[\frac{0.03}{0.082 \times 700}\right]$$

$K_C = 5.23 \times 10^{-4}$

14. (d) $SO_2(g) + \dfrac{1}{2}O_2(g) \rightleftharpoons SO_2(g);\qquad K_p = 4 \times 10^{-3}$

$SO_3 \rightleftharpoons SO_2(g) + \dfrac{1}{2}O_2(g);\qquad K'_p = \dfrac{1}{K_p}$

$2SO_3 \rightleftharpoons 2SO_2 + O_2(g);\qquad K'_p = \left(\dfrac{1}{4 \times 10^{-3}}\right)$

$$K''_p = (K'_p)^2\left[\frac{1}{4 \times 10^{-3}}\right]^2 = \left[\frac{1000}{4}\right]^2 = 6250 = 625 \times 10^2$$

$= 6.25 \times 10^4$ atm

15. (a) $\log\dfrac{K_2}{K_1} = \dfrac{\Delta H°}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

$$\log\frac{K_2}{0.0118} = \frac{597.4 \times 10^3}{2.303 \times 8.314}\left[\frac{1}{1300} - \frac{1}{1200}\right]$$

$\log K_2 = -2 + \log(0.0118) = -3.928 \Rightarrow K_2 = 1.18 \times 10^{-4}$

Therefore, option (A) is correct.

16. (c) $\Delta G° = \Delta H° - T\,\Delta S°;\ \Delta H° = -29.8 \times 10^3$ cal

$\Delta S° = -0.1 \times 10^3$ cal

$\Delta G° = -29.8 \times 10^3 - [-0.1 \times 10^3 \times 298]$

$\Delta G° = \Delta G + 2.303\,RT \log_{10} K_c$

ΔG = zero at equilibrium

$\Delta G° = -2.303\,nRT \log_{10} K_c$

$K_c = 1$

$$\log_{10} K_c = \frac{-\Delta G°}{2.303 \times RT}$$

$$= \frac{0}{2.303 \times 8.314 \times 298}$$

$\log_{10} K_c = 0 \Rightarrow K_c = 1$

17. (d)

$$\begin{array}{ccccccc} CH_3COOH & + & C_2H_5OH & \rightleftharpoons & CH_3COOC_2H_5 & + & H_2O \\ 1 & & 1 & & 0 & & 0 \\ 1-0.666 & & 1-0.666 & & 0.666 & & 0.666 \end{array}$$

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{[0.666][0.666]}{[0.333][0.333]} = 4$$

(a) Let x moles of ester is formed from 1 mole of acid and 0.5 mole of alcohol, then

$$K_C = \frac{x^2}{(1-x)(0.5-x)}$$

$$\frac{x^2}{(1-x)(0.5-x)} = 4 \Rightarrow x = 0.43$$

(b) $K_C = \frac{x^2}{(1-x)(4-x)}$ or $4 = \frac{x^2}{(1-x)(4-x)} \Rightarrow x = 0.93$

18. (d) $Q = \dfrac{\dfrac{n^{2+}_{\text{cm}}}{V}}{\left(\dfrac{\text{h}^{+}_{\text{of}}}{V}\right)^2} = \dfrac{n^{2+}_{\text{cn}}}{n^2\text{Ag}^+} \times \text{V}$

Backward direction

$$K_C = \frac{x}{\left(\frac{y}{0.5}\right)^2} \Rightarrow \frac{x \times 0.5^2}{y^2}$$

$$2\text{Ag}^+ + \text{Cu} = \text{Cu}^{2+} + 2\text{Ag}$$

As V is doubled $[\text{Cu}^{2+}]_{\text{eq}} < \frac{x}{2}$

19. (b) Extent of reaction can be calculated by the value of K_C. Higher the value of K_C, larger the extent of reaction.

(i) $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$

$$\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{0.01 \times 0.01}{0.01} = 0.01$$

(ii) $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2,\ K_C = \dfrac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$

$$= \frac{(0.01)^2}{(0.01)(0.01)} = 1$$

(iii) $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

$$K_C = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.01)^2}{(0.01)^4} = \frac{10000}{0.01 \times 0.01} = 1000$$

Extent of reaction I < II < III.

Multiple Correct Answers Type

20. (a, c, d)

For the reaction, $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

At 400 K, $K = 50$

At 500 K, $K = 1700$

(a) As the value of K increase with increase of temperature and $K = \frac{K_f}{K_b}$, this means that K_f increases, i.e., forward reaction is favoured. Hence, reaction is endothermic.

(c) Since, number of moles of gaseous products are greater than the number of moles of gaseous reactants. Thus, higher pressure favours the backward reaction, i.e., more $\text{N}_2\text{O}_4(g)$ will be obtained, if $P_{\text{product}} > P_{\text{reactant}}$.

(d) As reaction is accompanied by increases in the number of moles, entropy increases.

21. (a, c, d)

$$Q = \frac{[\text{S}_2]^4}{[\text{S}_8]} = \frac{(0.2)^4}{[2]} = 8 \times 10^{-4},\ K_C = 6.3 \times 10^{-6}$$

$$K_p = K_c \times (RT)^{\Delta n}$$
$$= 6.3 \times 10^{-6} \times (0.0821 \times 900)^3 = 2.55$$

Thus, reaction proceeds in backward direction, since Q > K_C.

22. (a, b, c)

From given reactions

(i) = –(iii) ; $\frac{1}{2}$(i) = –(iv); $\frac{1}{2}$(iii) = –(ii)

Matching Column Type

23. (d) For a reaction $\text{A} \rightleftharpoons \text{B} + \text{C}$

The reaction quotient $Q_C = \dfrac{[\text{B}][\text{C}]}{[\text{A}]}$

- If $Q_C < K_C$, the net reaction goes from left to right
- If $Q_C > K_C$, the net reaction goes from right to left
- If $Q_C = K_C$, no net reaction occurs.

Integer Type

24. (4) $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g);\quad K_c = 0.25$

For: $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g);\quad K_c = \frac{1}{0.25} = 4$

25. (1) $4\text{NH}_3(g) + 5\text{O}_2(g) \rightleftharpoons 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$

$$K = \frac{p^4_{\text{NO}} \times p^6_{\text{H}_2\text{O}}}{p^4_{\text{NH}_3} \times p^5_{\text{O}_2}} = \frac{(\text{bar})^{10}}{(\text{bar})^9} = (\text{bar})^1 \quad \therefore n = 1$$

26. (2) $\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$

$K_P = p_{\text{NH}_3} \times p_{\text{HCl}}$

$81 = p^2$

$p = 9$ atm

Total pressure = $p_{\text{NH}_3} \times p_{\text{HCl}} = 18$ atm

Thus, total pressure is 2 times the pressure of NH_3.

Comprehension Type

27. (b) Slope = $\dfrac{-\Delta\text{H}^\circ}{2.3R} = \dfrac{230}{2.3 \times 2} = -50$

28. (b) Using equation, $\log K = -\dfrac{\Delta\text{H}^\circ}{2.3RT} + \dfrac{\Delta\text{S}^\circ}{2.3R}$

29. (b) Using equation $\log\dfrac{K_2}{K_1} = \dfrac{\Delta\text{H}^\circ}{2.30R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

DPP 6.3

Subjective Type

1. (a) decrease (b) increase (c) decrease (d) increase
(e) increase (f) no change (g) increase (h) increase
(i) no change (j) no change

2. (a) Low, *T*, High *P*, excess of N_2 and H_2.
(b) High *T*, any *P*, excess of N_2 and O_2
(c) Low *T*, Low *P*, excess of C and H_2O
(d) High *T*, Low *P*, excess of N_2O_4.

3. (i) The reaction will move in the backward direction
(ii) No effect
(iii) The reaction will move in the backward direction
(iv) The reaction will move in the forward direction
(v) The reaction will move in the backward direction
(vi) The reaction will move in the backward direction

Single Correct Answer Type

4. **(b)** On adding CO, equilibrium (i) will shift backward. Hence concentration of Cl_2 will decrease. Decrease in concentration of Cl_2 will shift equilibrium (i) in the forward direction, i.e., more PCl_5 will dissociate. Hence, concentration of PCl_5 will decrease.

5. **(a)** As volume remains constant, the concentration of the three gases will remain unchanged on adding helium.

6. **(c)** Solid $\xrightarrow{\text{Heat}}$ liquid
ice
(more volume) (less volume)
Amount of liquid increases. Thus reaction goes toward less volume.

7. **(a)** In the reaction,

$$\underset{\text{(Pink)}}{[Co(H_2O_6)]^{3+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{(Blue)}}{[CoCl_4]^{2-}(aq)} + 6H_2O(l)$$

On cooling, the equilibrium shifts backward direction or on heating, the equilibrium shifts forward direction. Hence, reaction is endothermic, i.e., $\Delta H > 0$.

8. **(a)** In the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
If the total pressure, at which the equilibrium is established, is increased without changing the temperature, *K* will remain same. *K* changes only with change in temperature.

9. **(b)** For any physical equilibrium on increasing pressure equilibrium shifts in the direction of higher density.

10. **(b)** Addition of inert gas at constant volume has an effect on equilibrium concentrations.

11. **(b)** $H_2O(l) \rightleftharpoons H_2O(g)$
$K_p = (P_{H_2O})$
When neon is added at constant pressure, we have to increase volume of the container. So more water will evaporate to maintain equilibrium.

Multiple Correct Answers Type

12. **(b, c, d)**
Cu(I) forms insoluble compounds CuCl, CuCN and CuSCN. Hence, in the presence of Cl^-, CN^- and SCN^-, the equilibrium shifts in the backward direction.
In fact, Cu^{2+} ions combine with CN^- and SCN^- to form compounds which are not stable and dissociate to form Cu^+ compounds/complexes,
e.g., $Cu^{2+} + 2CN^- \rightarrow Cu(CN)_2$
$Cu(CN)_2 \rightarrow 2CuCN + (CN)_2$
$CuCN + 3CN^- \rightarrow [Cu(CN)_4]^{3-}$
$Cu^{2+} + 4SCN^- \rightarrow [Cu(SCN)_4]^{2-}$
Similarly, Cu^{2+} also combines with Cl^- ions to form $CuCl_2$ which reacts with Cu to form CuCl, thereby, shifting the equilibrium in the backward direction $CuCl_2 + Cu \rightarrow 2CuCl$.

13. **(a, b, d)**
ΔH is dependent on T. ΔH varies with temperature according to Kirchoff's equation. Hence, (a) is correct.
Equilibrium constant of a reaction depends only on temperature and is independent of the amount of $CaCO_3$. Hence, (b) is correct.
For the given reaction, $K = P_{CO_2}$ at a given T. Thus, *K* is independent of pressure. Hence, (c) is incorrect.
Catalyst only lowers the activation energy barrier and does not affect the value of ΔH. Hence, (d) is correct.

14. **(c, d)**
Addition of solids have no effect on equilibrium and temperature favours endothermic reaction while increasing pressure will shift equilibrium in backward direction as Δn_g is +ve.

15. **(a, c)**
Addition of solids have no effect on equilibrium and temperature favours endothermic direction while increasing pressure will shift equilibrium in backward direction as Δn_g is +ve.

16. **(b, c)**
Yield of product cannot be increased on increasing pressure that means reaction is Endothermic (ΔH = +ve).
$\Delta n = 2 : NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$
$\Delta n = 1 : N_2O_4(g) \rightleftharpoons 2NO_2(g)$

17. **(b, c, d)**

$$\therefore K_p = \frac{P_{PCl_3(g)} \times P_{Cl_2(g)}}{P_{PCl_5(g)}} = \frac{(n_{PCl_3(g)})_{eq.} \times (P_{Cl_2(g)})_{eq.}}{V \times (n_{PCl_5(g)})_{eq.}}$$

and on adding inert gas at constant pressure effect on equilibrium will be similar to as if volume of container has been increased.

18. **(a, b)**
$2A(g) + B(g) \rightleftharpoons 2C(g)$, $\Delta H = 13.6$ kJ
ΔH = +ve, thus endothermic reaction.
T↑ P↓
ΔH = –ve, thus exothermic reaction.
Δn = +ve T↓ P↑

Matching Column Type

19. **(a→r), (b→r), (c→q), (d→p)**
(A) Δn_g is +ve so as P is increased, backward shifting will take place. Total pressure even after shifting will remain same.
(B) Δn_g is –ve, so as V is increased, backward shifting will take place. But $P_{final} < P_{initial}$.
(C) No change but $P_{final} < P_{initial}$ as volume has increased.
(D) Forward shifting will take place and $P_{final} < P_{initial}$.

Comprehension Type

20. **(d)** Solubility of gas is favourable at high pressure and this process is exothermic, hence solubility will be more at low temperature.

21. **(c)** Since density of gold decreases after melting, therefore it is favourable at low pressure and high temperature.

22. (a, b)

Number of moles will remain unchanged but due to decreased volume. Pressure will get increased and also the concentrations.

DPP 6.4

Subjective Type

1. For the dissociation reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$\begin{array}{lcc} & N_2O_4(g) & 2NO_2(g) \\ \text{Initial moles} & 1 & 0 \\ \text{Moles at eq.} & 1-0.310 = 0.69 & 2 \times 0.310 \\ & & = 0.62 \end{array}$$

$(\alpha = 0.210, \text{ Given})$

Total $= 0.69 + 0.62$ $= 1.31$ moles

At one atmospheric pressure,

$$p_{N_2O_4} = \frac{0.69}{1.31} \times 1 \text{ atm}, \qquad p_{NO_2} = \frac{0.62}{1.31} \times \text{atm}$$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{(0.62/1.31 \text{ atm})^2}{(0.69/1.31 \text{ atm})} = 0.425 \text{ atm}$$

At 10 atmospheric pressure, suppose degree of dissociation $= \alpha$. Then

$$\begin{array}{lccc} & N_2O_4 & \rightleftharpoons & 2NO_2 \\ \text{Initial moles} & 1 & & 0 \\ \text{Moles at eq.} & 1-\alpha & 2\alpha, & \text{Total} = 1+\alpha \end{array}$$

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha} \times 10 \text{ atm}, \quad p_{NO_2} = \frac{2\alpha}{1+\alpha} \times 10 \text{ atm}$$

$$K_p = \frac{[20\alpha/(1+\alpha)]^2}{[10(1-\alpha)/(1+\alpha)]} = \frac{40\alpha^2}{1-\alpha(1+\alpha)} = \frac{40\alpha^2}{1-\alpha^2}$$

$$\therefore \quad \frac{40\alpha^2}{1-\alpha^2} = 0.425$$

Neglecting α^2 in comparison to 1, $40\alpha^2 = 0.425$ or $\alpha = 0.103$
$= 10.3\%$

2. Molar mass of $N_2O_4 = 28 + 64 = 92 \text{ g mol}^{-1}$

$$\begin{array}{lcc} & N_2O_4 \quad \rightleftharpoons & 2NO_2 \\ \text{Initial moles} & \frac{10}{92} & 0 \\ \text{After dissociation} & \frac{10}{92} - \frac{70}{100} \times \frac{10}{92} & 2 \times 0.076 \\ & = 0.109 - 0.076 & = 0.152 \\ & = 0.033 & \end{array}$$

$\therefore$ Total moles after dissociation $= 0.033 + 0.152 = 0.185$,
$T = 77°C = 77 + 273 \text{ K} = 350 \text{ K}$

$$PV = nRT$$

$$\text{or} \quad V = \frac{nRT}{P}$$

$$= \frac{0.185 \text{ moles} \times 0.0821 \text{ L atm K}^{-1} \text{mol}^{-1} \times 350 \text{ K}}{1 \text{ atm}}$$

$$= 5.32 \text{ L}$$

3. $LiCl.3NH_3(s) \rightleftharpoons LiCl.NH_3(s) + 2NH_3(g)$
$K_p = 9 \text{ (atm)}^2$

$$\begin{array}{lccc} & LiCl.NH_3(s) + & 2NH_3(g) \rightleftharpoons & LiCl.3NH_3(s) \\ t = 0 & 0.1 & a & 0 \end{array}$$

$$K_{p_1} = \frac{1}{9} \text{ (atm)}^{-2}$$

$$\begin{array}{lccc} t = ? & 0 & (a-0.2) & 0.1 \end{array}$$

Initially mole of $NH_3(a)$ should be added to bring in completion of reaction.

$$K_{p_1} = \frac{1}{P'(NH_3)^2}$$

$$\frac{1}{9} = \frac{1}{P'(NH_3)^2}$$

$$P'_{NH_3} = 3 \text{ atm}$$

$$PV = nRT$$
$$3 \times 5 = n \times 0.0821 \times 313$$
$$n = 0.5837$$
$$(a - 0.2) = 0.5837$$

Mole of $NH_3 = a = 0.5837 + 0.2$
$= 0.7837$ mole of NH_3 should be added for completion of reaction.

4.
$$\begin{array}{lccc} & 2AB_2(g) \rightleftharpoons & 2AB(g) \quad + & B_2(g) \\ t = 0 & a & 0 & 0 \\ & a(1-\alpha) & (a\alpha) & \frac{(a\alpha)}{2} \end{array}$$

$$\text{Total mole} = a\left[1 - \alpha + \alpha + \frac{\alpha}{2}\right] \qquad \frac{a[2+\alpha]}{2}$$

$$P_{AB_2} = \frac{a(1-\alpha) \times 2}{a(2+\alpha)} \times P; \qquad P_{AB} = \frac{a\alpha \times 2}{a(2+\alpha)} \times P$$

$$P_{B_2} = \frac{\left(\frac{a\alpha}{2}\right)}{\frac{a(2+\alpha)}{2}} = \left[\frac{\alpha}{2+\alpha}\right] \times P$$

$$K_P = \frac{\left(\frac{2\alpha}{2+\alpha} \times P\right)^2 \left(\frac{\alpha}{2+\alpha} \times P\right)}{\left(\frac{2(1+\alpha)}{2+P} \times P\right)^2}$$

$\alpha << 1$

$$K_P = \frac{\alpha^3 P}{2}; \quad \alpha = \left(\frac{2K_P}{P}\right)^{1/3} \quad \text{i.e., } x = \left(\frac{2K_P}{P}\right)^{1/3}$$

5. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
$$\begin{array}{cc} a(1-\alpha) & 2a\alpha \end{array}$$

(a) $M_{ab} = 38.33 \times 2 = 76.66$

(b) $$76.66 = \frac{a(1-\alpha) \times 92 + 2a\alpha \times 46}{a(1+\alpha)}$$

$\Rightarrow \quad \alpha = 0.2$

(c) $$\% \text{ of } NO_2 = \frac{2a\alpha}{a(1+\alpha)} \times 100 = 33.33\%$$

(d) $$K_P = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha} \times 2\right)^2}{\left(\frac{1-\alpha}{1+\alpha} \times 2\right)} = 0.33$$

6. (a) $n_{CO_2} = n_{H_2} = 0.338$ mole, $n_{CO} = n_{H_2O} = 0.112$ mole

(b) $n_{CO_2} = n_{H_2} = 0.594$ mole, $n_{CO} = n_{H_2O} = 0.197$ mole

$$\begin{array}{lccccccc} & CO_2(g) & + & H_2(g) & \rightleftharpoons & CO(g) & + & H_2O(g); \quad K_c = 0.11 \\ t=0 & 0.45 & & 0.45 & & & & \\ t=t_{eq.} & 0.45-x & & 0.45-x & & x & & x \end{array}$$

$$0.11 = \left(\frac{\dfrac{x/v}{0.45-x}}{v}\right)^2 \Rightarrow \frac{x}{0.45} = 0.33 \Rightarrow x = 0.11$$

(i) $n_{CO_2} = n_{H_2O} = 0.11; \quad n_{CO_2} = n_{H_2} = 0.34$

(ii)
$$\begin{array}{ccccccc} CO_2(g) & + & H_2(g) & \rightleftharpoons & CO(g) & + & H_2O(g) \; ; \; K_c = 0.11 \\ 0.34 & & 0.34 & & 0.11 & & 0.11 \\ 0.68 & & 0.68 & & 0.11 & & 0.11 \quad Q_c < K_c \\ 0.68-x & & 0.68-x & & 0.11-x & & 0.11+x \end{array}$$

$$0.11 = \left(\frac{0.11+x}{0.68-x}\right)^2 \Rightarrow \frac{0.11+x}{0.68-x} = 0.33 = \frac{1}{3} \Rightarrow 0.33 + 3x = 0.68 - x$$

$\Rightarrow \; 4x = 0.35x = 0.0875; \; n_{CO} = n_{H_2O} = 0.1975$

$n_{CO_2} = n_{H_2} = 0.5925$

Single Correct Answer Type

7. (d)

$$\begin{array}{lccccc} & A_2 & + & B_2 & \rightleftharpoons & 2AB \\ \text{mole of } t = 0 & 2 & & 4 & & 0 \\ \text{At eq.} & (2-x) & & (4-x) & & 2x \end{array}$$

Total volume at equilibrium is 1 + 3 = 4 litre

$$\therefore K_C = 4 = \frac{\left[\frac{2x}{4}\right]^2}{\left[\frac{2-x}{4}\right]\left[\frac{4-x}{4}\right]} = \frac{4x^2}{8-6x+x^2} = 4$$

$\therefore 4x^2 = 32 - 24x + 4x^2$

$$\therefore x = \frac{32}{24} = \frac{4}{3} = 1.33$$

$$\therefore [AB] = \frac{2 \times 1.33}{4} = 0.66$$

8. (a)

$$\begin{array}{lccccc} & N_2(g) & + & 3H_2 & \rightleftharpoons & 2NH_3 \\ \text{Initial mole} & 0.2 & & 0.6 & & \text{Total moles present} = 0.8 \\ \text{Mole of eq.} & (0.2-0.02) & & (0.6-0.06) & & \\ & 0.18 & & 0.54 & & 0.04 \end{array}$$

10% of the reactant i.e., 0.08 mole react. Let x mole of N_2 and $3x$ mole of H_2 react, then

$\therefore \quad 4x = 0.08$

$x = 0.02$

Total mole at eq. = 0.18 + 0.54 + 0.04 = 0.76

$$\therefore \frac{\text{Mole at } t=0}{\text{Mole at eq.}} = \frac{0.80}{0.76} = 1.05$$

Under similar conditions of P and T, this is also volume ratio.

9. (b) $\alpha = \left[\dfrac{D-d}{d}\right]; \quad \alpha = \left[\dfrac{D}{d} - 1\right]; \quad \left(\dfrac{D}{d}\right) = \alpha + 1.$

$\alpha = \dfrac{D-d}{(n-1)d}; \quad \alpha = \dfrac{D-d}{d}; \quad \alpha = \left(\dfrac{D}{d}\right) - 1.$

The point at which $\alpha = 0$.

$\left[\dfrac{D}{d} - 1\right] = 0; \quad \text{So,} \left(\dfrac{D}{d}\right) = 1.$

10. (a) NH_3 formed $= 5 \times \dfrac{100}{1000} = 0.5$ mole

$$\begin{array}{ccccc} N_2 & + & 3H_2 & \rightleftharpoons & 2NH_3 \\ 1-0.25 & & 3-0.75 & & 0.5 \end{array}$$

$$\therefore \quad K_C = \frac{0.5^2}{0.75 \times (2.25)^3}$$

11. (b)

$$\begin{array}{lccccc} & 2NOBr(g) & \rightleftharpoons & 2NO(g) & + & Br_2(g) \\ \text{at eq.} & P - \frac{2P}{9} = \frac{6P}{9} & & \frac{2P}{9} & & \frac{P}{9} \end{array}$$

$$P_T = \frac{6P}{9} + \frac{2P}{9} + \frac{P}{9} = P$$

$$K_P = \frac{\left(\frac{2P}{9}\right)^2 \times \left(\frac{P}{9}\right)}{\left(\frac{6P}{9}\right)^2} = \frac{K_P}{P} = \frac{1}{81}.$$

12. (d)

$$\begin{array}{ccccc} 2HI & \rightleftharpoons & H_2 & + & I_2 \\ P & & 0 & & 0 \\ P(1-\alpha) & & \frac{P\alpha}{2} & & \frac{P\alpha}{2} \end{array}$$

$$K_P = \frac{P^2\alpha^2}{4(1-\alpha)^2}$$

$$K_P = \left(\frac{\alpha}{2(1-\alpha)}\right)^2$$

$$\frac{\alpha}{2(1-\alpha)} = \sqrt{K_P}$$

$$\frac{\alpha}{1-\alpha} = 2\sqrt{K_P}$$

$$\frac{1-\alpha}{\alpha} = \frac{1}{2\sqrt{K_P}}$$

$$\frac{1}{\alpha}-1=\frac{1}{2\sqrt{K_P}}$$

$$\frac{1}{\alpha}=\frac{1}{2\sqrt{K_P}}+1$$

$$\frac{1}{\alpha}=\frac{1+2\sqrt{K_P}}{2\sqrt{K_P}}$$

$$\alpha=\frac{2\sqrt{K_P}}{1+2\sqrt{K_P}}$$

13. (b) $SO_3(g) \rightleftharpoons SO_2(g)+\frac{1}{2}O_2(g)$

$$M_{mix}=\frac{0.9\times0.082\times1000}{1.23}=60$$

$1-\alpha \qquad \alpha \qquad \frac{\alpha}{2}$

$$M_{mix}=\frac{\alpha\cdot M_{SO_2}+\frac{\alpha}{2}\cdot M_{O_2}+(1-\alpha)M_{SO_3}}{1+\frac{\alpha}{2}}$$

$$1+\frac{\alpha}{2}=\frac{80}{60} \Rightarrow \frac{\alpha}{2}=\frac{20}{60}$$

$$\Rightarrow \alpha=\frac{2}{3}$$

14. (d)

$$\begin{array}{lccccl} & Ni^{2+} & + & 6NH_3 & \rightarrow & [Ni(NH_3)]^{+6} \quad K_f=6\times10^8 \\ t=0 & 0.01\text{ mole} & & 0.1\text{ mole} & & 0 \end{array}$$

$$K_c=\frac{[Ni(NH_3)_6^{+6}]}{[Ni^{+2}][NH_3]^6}=\frac{(0.1)}{[Ni^{2+}](0.4)^6}=6\times10^8\ [Ni^{2+}]=4\times10^{-8}.$$

15. (a) $\frac{VD_i}{VD_e}=\frac{n_e}{n_i}$

$\frac{46}{30}=(1+\alpha)$

$1.533=1+\alpha$

$\alpha=0.533$

% dissociation = 53.3%

Multiple Correct Answers Type

16. (a, b)

We know that

$$d=\frac{D}{1+(n-1)\alpha}$$

where n is the number of mole of gases produced from one mole of a gas.

17. (b, c, d)

$$\begin{array}{lcc} & N_2O_4 \rightleftharpoons & 2NO_2 \\ t=0 & a & 0 \\ t & a(1-\alpha) & 2a\alpha \end{array}$$

Vapour density $=\frac{46}{1+\alpha}=30.67$

So, $1+\alpha=1.6=0.5=59\%$

Total pressure $=\frac{1.5\times1.5\times0.082\times300}{8.2}=6.75$ atm

So, $K_P=\frac{4\alpha^2}{1-\alpha^2}P=9$ atm

$\Rightarrow$ and for density of mixture $\frac{138}{8.2}$ g/L $=16.83$ g/L

Matching Column Type

18. (a → q), (b → q), (c → s), (d → p)

(i) $NH_3 \rightleftharpoons \frac{1}{2}N_2+\frac{3}{2}H_2$

No. of moles before dissociation	1	0	0
No. of moles after dissociation	$1-\alpha$	$\frac{1}{2}\alpha$	$\frac{3}{2}\alpha$
Total moles	$1-\alpha+\frac{1}{2}\alpha+\frac{3}{2}\alpha=1+\alpha$		

$\therefore \quad \alpha=\frac{D-d}{d}$

(ii) $N_2O_4 \rightleftharpoons 2NO_2$

No. of moles before dissociation	1	0
No. of moles after dissociation	$1-\alpha$	2α
Total moles	$1-\alpha+2\alpha=1+\alpha$	

$\therefore \quad \alpha=\frac{D-d}{d}$

(iii) $PH_3 \rightleftharpoons \frac{1}{4}P_4+\frac{6}{4}H_2$

No. of moles before dissociation	1	0	0
No. of moles after dissociation	$1-\alpha$	$\frac{1}{4}\alpha$	$\frac{6}{4}\alpha$
Total moles	$1-\alpha+\frac{1}{4}\alpha+\frac{6}{4}\alpha=1+\frac{3}{4}\alpha$		

$\therefore \quad \alpha=\frac{4(D-d)}{3d}$

(iv) $A \rightleftharpoons \frac{6}{5}B+\frac{9}{5}C$

No. of moles before dissociation	1	0	0
No. of moles after dissociation	$1-\alpha$	$\frac{6}{5}\alpha$	$\frac{9}{5}\alpha$
Total moles	$1-\alpha+3\alpha=1+2\alpha$		

$\therefore \quad \alpha=\frac{(D-d)}{2d}$

Integer Type

19. (1)

$$\begin{array}{lcccc} & A(g)+ & B(g) \rightleftharpoons & C(g)+ & D(g) \\ t_0 & 4 & 4 & 0 & 0 \\ t_{eq} & 4-2 & 4-2 & 2 & 2 \end{array}$$

$$K_c=\frac{[C][D]}{[A][B]}=\frac{2\times2}{2\times2}=1$$

20. (6) $PV = nRT$

$1 \times 8.96 = N \times 0.0821 \times 473$

$n = 0.23$

$NH_3COONH_4(s) \rightarrow 2NH_3(g) + CO_2(g)$

$$n_{NH_2COONH_4} = \frac{0.23}{3} = 0.0767$$

Mass of $NH_2COONH_4 = 0.0767 \times 74$
$= 6$ g

Comprehension Type

21. (a) $2NH_3 \rightleftharpoons N_2 + 3H_2$

10	0	0	at 300 K
$(10 - 2x)$	x	$3x$	at 620 K

Pressure increases due to increase in temperature as well as due to increase in mole.

Initially $P \propto T$

$\therefore \quad 15 \propto 300$

$\therefore \quad P = \frac{620}{300} \times 15 = 31$ atm of 10 mole of NH_3 at 620 K

Now, NH_3 is dissociated to attain 50 atm at 620 K.

Thus, $P \propto n$ or $10 \propto 31$

$10 + 2x \propto 50$

$\therefore \quad 2x = 6.13$

$$\therefore \quad \alpha = \frac{2x}{10} \times 100 = \frac{6.13 \times 100}{10} = 61.3\%$$

22. (d) $K_p = \frac{n_{N_2} \times (n_{H_2})^3}{(n_{NH_3})^2} \times \left[\frac{P}{\Sigma n}\right]^2$

$$= \frac{\frac{6.13}{2} \times \left[\frac{6.13 \times 3}{2}\right]^3}{[10 - 6.13]^2} \times \left[\frac{50}{10 + 6.13}\right]^2 = 1.528 \times 10^3 \text{ atm}^2$$

23. (a) $PV = nRT$

$15 \times V = 10 \times 0.0821 \times 300$

$\therefore \quad V = 16.42$ litre

24. (c) Increase in pressure favours the reaction showing decrease in volume, i.e., backward reaction and increase in temperature favours endothermic reaction, i.e., forward one.

25. (d) $\text{V. D.} = \frac{\text{Molar mass}}{2}$

$$= \frac{3.87 \times 17 + \frac{6.13}{2} \times 28 + \frac{6.13}{2} \times 3 \times 2}{2 \times \left[3.87 + \frac{6.13}{2} + \frac{6.13}{2} \times 3\right]} = 5.27$$

26. (b) $\Delta H = \Delta U + \Delta nRT$

$\therefore \Delta U = 91940 - 2 \times 8.314 \times 620 = 81630.6$ J

27. (a) $2.303 \log \frac{K_{P_2}}{1.53 \times 10^3} = \frac{91940}{8.314}\left[\frac{-100}{620 \times 520}\right]$

$\therefore \quad K_{P_2} = 49.58 \text{ atm}^2$

28. (c) $\alpha = \frac{D - d}{d(n - 1)}$

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$n = 2$

$$\alpha = \frac{104.25 - 70.2}{70.2} \left[n = \frac{\text{product mole}}{\text{reactant mole}}\right]$$

$$\alpha = \frac{34.05}{70.2} = 0.485$$

$\alpha = 0.485 \rightarrow 200°C$

$$\alpha = \frac{104.25 - 57.2}{57.2} = \frac{47.05}{57.2}$$

$\alpha = 0.822 \rightarrow 252°C$

$$\frac{K_{a_1}}{K_{a_2}} = \frac{C\alpha_1^2}{C\alpha_2^2} = \frac{0.235}{0.676}$$

$$\frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1^2}{\alpha_2^2}$$

$$\frac{K_{a_1}}{K_{a_2}} = \frac{0.235}{0.676}$$

29. (a) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$\Delta n = 2 - 1 = 1$

$\Delta H = +$ve Endothermic reaction

With increasing temperature dissociation constant; Increases, thus $\rightarrow \alpha\uparrow$ $d\downarrow$, it is endothermic reaction [$T\uparrow P\downarrow$].

30. (c) $\alpha = \frac{D - d}{d(n - 1)}$ $\quad d < D$ always

α = must be (+ve) value. $\quad d$ = V.D. of mixture

D = V.D. of pure state

DPP 6.5

Subjective Type

1. $A(s) \rightleftharpoons B(g) + C(g)$ $\quad K_{p1} = 300$

— $\quad P_1 \quad (P_1+P_2)$ $\quad K_{p1} = P_1\,(P_1 + P_2)$

$D(s) \rightleftharpoons E(g) + C(g)$ $\quad K_{p2} = 600$

$P = 2 \quad P_1 + P_2$ $\quad K_{p2} = P_2\,(P_1 + P_2)$

$$\left(\frac{K_{p1}}{K_{p2}}\right) = \frac{P_1(P_1 + P_2)}{P_2(P_1 + P_2)}$$

$$\frac{300}{600} = \left(\frac{P_1}{P_2}\right)$$

$$\frac{P_1}{P_2} = \frac{1}{2} \quad \Rightarrow \quad P_2 = 2P_1$$

$K_{p1} = P_1(P_1 + P_2)$

$K_{p1} = P_1(P_1 + 2P_1)$

$300 - P_1(3P_1)$

$P_1^2 = 100 \qquad (P_1 = 10)$

$P_2 = 20$ atm

Now Total pressure

$= P_B + P_E + P_C$

$= (P_1 + P_2) + (P_1 + P_2) = (10 + 20) + (30) = 60$ atm.

2. $A(s) \rightleftharpoons A'(g) + H_2S(g)$ $B(s) \rightleftharpoons B'(g) + H_2S(g)$

$A(s) \rightleftharpoons A'(g) + H_2S(g) \quad P = 50\text{ mm}$

$\Rightarrow \quad P_{H_2S} = P_A = P/2 = 25\text{ mm}$

$B(s) \rightleftharpoons B'(g) + H_2S(g) \quad P = 68\text{ mm}$

$\Rightarrow \quad P_{H_2S} = P_B = P/2 = 34\text{ mm}$

(i) $K_{p1} = (25)^2 = 625\text{ mm}^2$

$K_{p2} = (34)^2 = 1156\text{ mm}^2$

(ii) Ratio of moles is same as that of partial pressure, so

$$\begin{array}{l} A(s) \rightleftharpoons A'(g) + H_2S(g) \\ \qquad\qquad P_1 \qquad P_1 + P_2 \end{array}$$

$$\begin{array}{l} B(s) \rightleftharpoons B'(g) + H_2S(g) \\ \qquad\qquad P_2 \qquad P_2 + P_1 \end{array}$$

$$K_{p1} = P_A \times P_{H_2S} = P_1 = (P_1 + P_2) \qquad \text{(i)}$$

$$K_{p1} = P_B \times P_{H_2S} = P_2 = (P_1 + P_2) \qquad \text{(ii)}$$

$$\frac{K_{P_1}}{K_{P_2}} = \frac{P_1}{P_2} = \frac{625}{1156}$$

(iii) Total pressure $= P_1 + P_2 + (P_1 + P_2) = 2(P_1 + P_2)$

$\text{(i)} + \text{(ii)} = (P_1 + P_2)^2$

$$\sqrt{K_{p_1} + K_{p_2}} = P_1 + P_2$$

$$P_T = 2 \times K_{p_1}(\sqrt{K_{p_1} + K_{p_2}}) = 84.4\text{ mm.}$$

3. $K_{p_1} = \dfrac{1}{20P_0^2}, K_{p_2} = \dfrac{3}{20P_0^2}$

$$\begin{array}{cccc} N_2(g) & + \quad 3H_2(g) & \rightleftharpoons & 2NH_3(g) \\ 9P - x - y & 13P - 3x - 2y & & 2x \\ N_2(g) & + \quad 2H_2(g) & \rightleftharpoons & N_2H_3(g) \\ 9P - x - y & 13P - 3x - 2y & & y \end{array}$$

Given $9P - x - y + 13P - 3x - 2y + 2x + y = 7P_o$

$$\Rightarrow \quad 22P - 2x - y = 7P_o \qquad (1)$$

then $2x = P_o \qquad (2)$

and $13P - 3x - 2y = 2P_o \qquad (3)$

$$22P - 2y = 5P_o$$

$$\begin{array}{r} +13P - 2y = +\frac{7}{2}P_o \\ - \qquad + \qquad - \\ \hline 9P = \frac{9}{2}P_o \end{array} \Rightarrow P = \frac{P_o}{2}$$

$$9P - x - y = \frac{9P_o}{2} - \frac{P_o}{2} - \frac{3P_o}{2} = \frac{5P_o}{2} \quad \Rightarrow \quad 2y = \frac{13 - 7}{2}P_o = 3P_o$$

$$13P - 3x - 2y = \frac{13P_o}{2} = \frac{3P_o}{2} - \frac{6P_o}{2} = 2P_o \quad \Rightarrow \quad y = \frac{3}{2}P_o$$

$$K_1 = \frac{(2x)^2}{(9P - x - y)(13P - 3x - 2y)^3} = \frac{P_o^2}{\frac{5}{2}P_o \cdot (2P_o)^3} = \frac{1}{20P_o^2}$$

$$K_2 = \frac{\frac{3}{2}P_o}{\left(\frac{5}{2}P_o\right)(2P_o)^2} = \frac{3}{20P_o^2}$$

Single Correct Answer Type

4. (b) $(P_{H_2O})^4 = 16 \times 10^{-12} \Rightarrow (P_{H_2O}) = 2 \times 10^{-3}$ atm

P_s at $= \dfrac{7.6}{760} = 1 \times 10^{-2}$ atm.

$$\text{which absorbed} = \frac{(1 \times 10^{-2} - 2 \times 10^{-3}) \times 1}{0.082 \times 274}$$

$$= 3.57 \times 10^{-4}\text{ mole}$$

$$\text{Mass} = 3.5 \times 10^{-4} \times 18 = 6.4 \times 10^{-3}\text{ g}$$

$$= 6.4\text{ mg}$$

5. (b) $(P_{H_2O})^4 = 16 \times 10^{-12} \Rightarrow (P_{H_2O}) = 2 \times 10^{-3}$ atm

$$\therefore \text{RH} < \frac{1.5 \times 10^{-2}}{\frac{22.8}{760}} \times 100 = 50\%$$

6. (d) $(P_{H_2O})^5 = 31.25 \times 10^{-13} \Rightarrow (P_{H_2O}) = 5 \times 10^{-5}$ atm.

7. (d) $AB \rightleftharpoons A^+ + B^- \qquad K_1 = \dfrac{(A^+) \cdot (B^-)}{AB}$

$AB + B^- \rightleftharpoons AB^-{}_2 \qquad K_2 = \dfrac{(AB_2^-)}{(AB)(B^-)}$

$$\frac{K_1}{K_2} = \frac{(A^+) \cdot (B^-)(AB) \times (B)^-}{(AB) \times (AB_2^-)}$$

$$\frac{K_1}{K_2} = \frac{(A^+)(B^-)^2}{(AB_2^-)}$$

$$\frac{1}{(B^-)^2} = \frac{(A^{+1})}{AB_2^-}$$

8. (a)

$$\begin{array}{l} AB \rightleftharpoons A^+ + B^-, K_1 \\ (z - y) \qquad y \qquad y - x \end{array}$$

$$\begin{array}{l} AB \quad + \quad B^- \rightleftharpoons AB_2^-, K_2 \\ (z - y) \quad (y - x) \qquad\quad x \end{array}$$

$$\frac{K_1}{K_2} = \frac{y(y - x)}{(z - y)} = \frac{(z - y)(y - x)}{x}(y - x)^2$$

Multiple Correct Answers Type

9. (a, c)

$$AB \rightleftharpoons \underset{y}{A^+} + \underset{y-x}{B^-}, \quad k_1$$

$$AB + \underset{y-x}{B^-} \rightleftharpoons \underset{x}{AB_2^-}, \quad k_2$$

$$\Rightarrow \quad k_1 = (y - x)y \qquad k_2 = \frac{x}{y - x}$$

$$\Rightarrow \quad \frac{k_1}{k_2} = \frac{y}{x}(y - x)^2$$

Comprehension Type

10. (c) $Na_2SO_4(s).10H_2O \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$

0°C and 4.58 torr $10H_2O$ molecule eliminate.

11. (a) For efflorescent – Interattraction force between molecules must be weak. For that condition, pressure will be low.

12. (b) 1 torr = 760 mm of Hg

Vapour pressure of water at 0°C = 4.58 torr

$$P = \frac{760 \times 4.58}{100} \text{ atm}$$

$P = 3.48$ atm V_{constant} = (closed vessel)

$P = nRT, \quad T = 0°\text{C} = 273$ K

$\therefore \quad 3.48 = n \times 22.4$

$\therefore \quad n = 0.15$ mole

$\therefore \quad 1$ mole = 142 g

$\therefore \quad 0.15$ mole = 142×0.15

= 21.3%

21.3% – Na_2SO_4 absorb moisture when exposed to air at 0°C.

CHAPTER 7

DPP 7.1

Subjective Type

1. $[H^+] = \sqrt{(3\times10^{-2}\times2\times10^{-4})+(10^{-1}\times1\times10^{-10})} = 3\times10^{-3}\text{ M}$

for HA, $[H^+] = [A^-] = 3\times10^{-3}\text{ M}$

for HB, $K_a = 10^{-10} = \dfrac{[H^+][B^-]}{[HB]}$

Therefore, $[B^-] = 3.33\times10^{-9}\text{ M}$

Hence, $[H^+] = [A^-] = 3\times10^{-3}\text{ M}$, $[B^-] = 3.33\times10^{-9}\text{ M}$

2. $[H^+] = \sqrt{(0.1\times2.4\times10^{-4})+(0.1\times4\times10^{-4})} = 8\times10^{-3}\text{ M}$

for HCOOH, $K_a = 2.4\times10^{-4} = \dfrac{[H^+][HCOO^-]}{[HCOOH]}$

Therefore, $[HCOO^-] = 3\times10^{-3}\text{ M}$

for HOCN, $K_a = 4\times10^{-4} = \dfrac{[H^+][OCN^-]}{[HOCN]}$

Therefore, $[OCN^-] = 5\times10^{-3}\text{ M}$

Hence, $[H^+] = 8\times10^{-3}\text{ M}$, $[HCOO^-] = 3\times10^{-3}\text{ M}$, $[OCN^-] = 5\times10^{-3}\text{ M}$

3. $HA \rightleftharpoons H^+ + H^-$

Applying Ostwald's dilution law for a weak acid,

$$\alpha = \sqrt{K_a V}$$

$$K_a = 4.0\times10^{-10},\quad V = \frac{1}{0.01} = 100\text{ litre}$$

$$\alpha = \sqrt{4\times10^{-10}\times10^2} = 2\times10^{-4}$$

Concentration of hydrogen ions

$$= \frac{\alpha}{V} = \frac{2\times10^{-4}}{100} = 2\times10^{-6}\text{ mol L}^{-1}$$

or Concentration of hydrogen ions

$$= \sqrt{CK_a} = \sqrt{0.01\times4\times10^{-10}} = 2\times10^{-6}\text{ mol L}^{-1}$$

4. According to Bronsted-Lowry concept, acid gives H^+ ion and base accept H^+ ion.

Acid	**Base**
(a) $[Al(H_2O)_6]^{3+}$	$[Cu(H_2O)_3(OH)]^+$
(b) $[Al(H_2O)_6]^{3+}$	$[Fe(H_2O)_5(OH)]^{2+}$
(c) H_2O	O^{2-}
(d) CH_3OH	H^-

5. i, v, vi

$HA\,(aq) + B^-\,(aq) \rightleftharpoons HB(aq) + A^-\,(aq)$; $K_{eq.} = 10^{-4}$

$K_{eq.}$ is very small, So reaction shifts in backward direction.

(1) HB is more stronger acid than HA.

(2) A^- is more stronger base than B^-.

(3) B^- and HB are conjugate acid-base pair.

6. $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ **(self ionisation)**

and $K = [NH_4^+][NH_2^-]$ $\therefore\ [NH_4^+] = [NH_2^-]$

$\therefore\ [NH_2^-] = \sqrt{K} = \sqrt{10^{-30}} = 10^{-15}\text{ M}$

Number of amide ions in $10^3\text{ cm}^3 = 10^{-15}\times6\times10^{23}$

$\therefore$ Number of amide ions in one $\text{cm}^3 = \dfrac{10^{-15}\times6\times10^{23}}{10^3}$

$= 6\times10^5$ ions

Single Correct Answer Type

7. (b) The corresponding acids are HI, HCl, HNO_2 and HCN. Their acid strength follows the order HI > HCl > HNO_2 > HCN. Hence, their conjugate base follows the reverse order.

8. (d) The conjugate acid-base pairs are (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH).

9. (a) The conjugate acids are H_2O, NH_3, $HC\equiv CH$ and CH_3CH_3. Their order of acid strength is $CH_3CH_3 < NH_3 < HC\equiv CH < H_2O$. Their conjugate base follows the reverse order.

10. (c)

$$x_1 = \sqrt{\frac{K_a}{C_1}}$$

$$x_2 = \sqrt{\frac{K_a}{C_1}}$$

$$\therefore\quad \frac{x_2}{x_1} = \sqrt{\frac{C_1}{C_2}}$$

$$x_2 = x_1\sqrt{\frac{C_1}{C_2}} = 1\times\frac{1}{2} = 0.5\%$$

11. (a) $BOH \rightleftharpoons\ + OH^-$

By Ostwald's dilution law,

$[OH^-] = \sqrt{K_b C}$

$1.5\times10^{-3} = \sqrt{1.5\times10^{-5}\times C}$

$\therefore\quad C = 0.15\text{ M}$

12. (b) In this solution, source of OH^- is water.

$$\therefore \quad C\alpha = [OH^-]$$

$$\alpha = \frac{10^{-9}}{1000/18} = 1.8 \times 10^{-11}\ M$$

$$\%\ \text{ionisation} = 1.8 \times 10^{-9}$$

Multiple Correct Answers Type

13. (d) Reaction proceeds in direction favouring weak acids and bases. So, CN^- is also a weaker base than OH^-.

14. (a, b, c, d)

15. (a, b)

H_2SO_4 is a strong acid and it is completely dissociated in H_2O. Hence its K_{a1} and K_{a2} are determined in CH_3COOH.

Also H_2SO_4 is neutral while HSO_4^- because the –ve charge has more affinity towards H^+ ion. Hence choices (a) and (b) are correct while (c) is incorrect. As H_2SO_4 is completely dissociated in water so a 0.01 M H_2SO_4 is completely dissociated and its $[H^+]$ ion conc. will be equal to 0.02 M.

Hence, choice (d) will be incorrect.

16. (a, c)

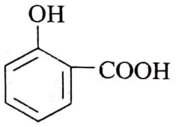
As K_a of acid increases, K_b of its conjugate base decreases.

Matching Column Type

17. (A→2, 3, 4, 5, 6), (B→1, 3), (C→3, 4, 6), (D→3, 4, 6), (E→4), (F→4)

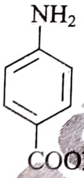
Lewis acid: Species which accepts electron pairs.

For example:

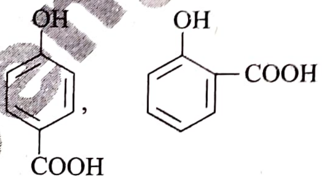


Lewis base: Species which donates e^- pairs molecules containing lone pairs act as Lewis base.

For example:



Lowry-Bronsted acids and bases: Acid is a substance that donate H^+ ions and bases are substance which accept H^+ ions. For example:

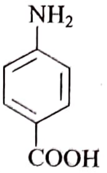


, $H_2PO_4^-$, HPO_4^{2-}

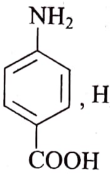
bases: HPO_3^{2-}, $H_2PO_2^-$

Zwitter ion is a neutral molecule with a positive and a negative electrical charge.

For example:



Amphiphotic: can either donate or accept a proton, thus acting either as an acid or base.



, $H_2PO_4^-$, HPO_4^{2-}

Integer Type

18. (7) $[H^{\oplus}]_{mix} = \sqrt{\Sigma K_{ai} C_i}$

$$= \sqrt{1.8 \times 10^{-4} \times 0.1 + 3.1 \times 10^{-4} \times 0.1}$$

$$= \sqrt{4.9 \times 10^{-5}}\ M = 7 \times 10^{-3}\ M$$

Thus x is 7.

19. (3) Amphiprotic – (ii), (iii), (v)

Acidic – (vi), (vii) ; Basic – (i), (iv)

Comprehension Type

20. (a) $\dfrac{\alpha_1}{\alpha_2} = \sqrt{\dfrac{c_2}{c_1}} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}}$

$$\frac{1}{2} = \sqrt{\frac{2 \times 10^{-4}}{K_{a_2}}}$$

$$\frac{1}{4} = \frac{2 \times 10^{-4}}{K_{a_2}}$$

$$K_{a_2} = 8 \times 10^{-4}$$

21. (a) $\dfrac{\alpha_1}{\alpha_2} = \sqrt{\dfrac{c_2}{c_1}} \Rightarrow \dfrac{0.00424}{\alpha_2} = \sqrt{\dfrac{0.1}{0.01}}$

$$\frac{0.00424}{\alpha_2} = \sqrt{10} = 3.19$$

$$\alpha_2 = \frac{0.00424}{3.19} = \frac{4.24 \times 10^{-3}}{3.19}$$

$$\alpha_2 = 1.33\%$$

22. (d) Relative strength of two monoprotic acids:

$$\text{Relative strength} = \frac{\text{strength of I acid}}{\text{strength of II acid}}$$

$$= \frac{[\mathrm{H^+}]\text{ furnished by I acid}}{[\mathrm{H^+}]\text{ furnished by II acid}} = \frac{C_1\alpha_1}{C_2\alpha_2}$$

$$= \frac{C_1}{C_2} \times \sqrt{\left(\frac{K_{a_1}\,C_2}{K_{a_2}\,C_1}\right)} = \sqrt{\left(\frac{K_{a_1}\,C_1}{K_{a_2}\,C_2}\right)}$$

$$= \sqrt{\left(\frac{K_{a_1}}{K_{a_2}}\right)} \qquad (\text{if } C_1 = C_2)$$

When pH of two acids are same :

$$[\mathrm{H^+}]_1 = [\mathrm{H^+}]_2$$

$$\mathrm{C_1\alpha_1 = C_2\alpha_2}$$

$$\frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$\frac{K_{a_1}}{K_{a_2}} = \frac{\mathrm{C_2}}{\mathrm{C_1}}$$

DPP 7.2

Subjective Type

1. For 10 ppm of SO_2 in the atmosphere, the partial molar volume of SO_2 in a total volume of 10^6 dm^3 of the atmospheric air will be equal to 10 dm^3. Its molar concentration in air would be

$$c = \frac{(10\mathrm{dm^3})/\{(22.414\ \mathrm{dm^3mol^{-1}})(298\mathrm{K})/(273\mathrm{K})\}}{10^6\,\mathrm{dm^3}}$$

$$= 4.087 \times 10^{-7}\,\mathrm{mol\ dm^{-3}}$$

This concentration is very much less than the given solubility of SO_2 in water. Hence, it may be assumed that the entire SO_2 in air will dissolve in rain water.

If the concentration x of dissolved SO_2 is present in the ionized form, we will have

$$\begin{array}{ccccc} \mathrm{H_2SO_3} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{HSO_3^-} \\ c-x & & x & & x \end{array}$$

Hence $K_a = \dfrac{[\mathrm{H^+}][\mathrm{HSO_3^-}]}{[\mathrm{H_2SO_3}]} = \dfrac{x^2}{c-x}$ or $x^2 + K_a x - K_a c = 0$ (1)

or $x = \dfrac{-K_a \pm \sqrt{K_a^2 + 4K_a c}}{2}$

It is given that $K_a^o = 10^{-1.92} = 0.012$

Substituting K_a and c in Eq. (1), we get

$$x = \frac{(-0.012\ \mathrm{M}) + \sqrt{(0.012\mathrm{M})^2 + 4(0.012\mathrm{M})(4.087 \times 10^{-7}\mathrm{M})}}{2}$$

$$= 4.08 \times 10^{-7}\,\mathrm{M}$$

that is, almost whole of dissolved SO_2 is present in the ionized form H^+ and HSO_3^-. This is to be expected since the concentration of dissolved SO_2 is very small (Ostward dilution law).

For this small concentration of H^+ from the dissolved SO_2, the contribution coming from the dissociation of water may not be negligible. Hence, in solution we will have

$$[\mathrm{H^+}]_{\text{total}} = [\mathrm{H^+}]_{\text{acid}} + [\mathrm{H^+}]_{\text{water}} = [\mathrm{H^+}]_{\text{acid}} + [\mathrm{OH^-}]_{\text{water}}$$

$$= [\mathrm{H^+}]_{\text{acid}} + \frac{K_w}{[\mathrm{H^+}]_{\text{total}}}$$

or $[\mathrm{H^+}]^2_{\text{total}} - [\mathrm{H^+}]_{\text{acid}} = [\mathrm{H^+}]_{\text{total}} - K_w = 0$

Solving for $[\mathrm{H^+}]_{\text{total}}$, we get

$$[\mathrm{H^+}]_{\text{total}} = \frac{[\mathrm{H^+}]_{\text{acid}} + \sqrt{[\mathrm{H^+}]^2_{\text{acid}} + 4K_w}}{2}$$

$$= \frac{(4.08 \times 10^{-7}\,\mathrm{M}) + \sqrt{(4.08 \times 10^{-7}\,\mathrm{M})^2 + 4(1 \times 10^{-14}\,\mathrm{M^2})}}{2}$$

$$= 4.31 \times 10^{-7}\ \mathrm{M}$$

Hence, pH = –log $\{[\mathrm{H^+}]/\mathrm{M}\}$ = –log $(4.31 \times 10^{-7}) = 6.37$

2.
$$\begin{array}{lcccc} & \mathrm{H_2O} & \rightleftharpoons & \mathrm{H^+} & + \ \mathrm{OH^-} \\ t = 0 & \mathrm{C} & & & \\ t_{\text{eq}} & \mathrm{C(1-\alpha)} & & \mathrm{C\alpha} & \mathrm{C\alpha} \end{array}$$

So, $[\mathrm{H^+}] = [\mathrm{OH^-}] = \mathrm{C\alpha} = \dfrac{1000}{\cdot 18} \times 3.6 \times 10^{-9}$

$\therefore$ pH = 7 – log 2 = 6.7 and $K_w = [\mathrm{H^+}][\mathrm{OH^-}] = 4 \times 10^{14}$

3. (a) Meq. of $Ca(OH)_2 = 20 \times 0.1 \times 2 = 4$

$\therefore$ Meq. of HCl $= 25 \times 0.1 \times 1 = 2.5$

Meq of Ca $(OH)_2$ left $= 4 - 2.5 = 1.5$

$\therefore$ $[\mathrm{Ca(OH)_2}] = \dfrac{1.5}{20 + 25} = \dfrac{1}{30}$ $\Rightarrow$ $[\mathrm{OH^-}] = \dfrac{2}{30} = \dfrac{1}{15}$

$\therefore$ pOH = log 15 = 1.18 $\qquad\therefore$ pH = 12.82

(b) Meq. of $H_2SO_4 = 10 \times 0.01 \times 2 = 0.2$.

$\therefore$ Meq. of $Ca(OH)_2 = 10 \times 0.01 \times 2 = 0.2$.

Solution is neutral and pH = 7.

(c) Meq. of $H_2SO_4 = 10 \times 0.1 \times 2 = 2$.

Meq. of KOH $= 10 \times 0.1 \times 1 = 1$

$\therefore$ Meq. of H_2SO_4 left = 1

$\therefore$ $[\mathrm{H_2SO_4}] = 1/20 = 5 \times 10^{-2}$

$\therefore$ $[\mathrm{H^+}] = 5 \times 10^{-2}$ and pH = 1.3

4. pH = 6

$[\mathrm{H^+}] = 10^{-6}$

$N_1V_1 = N_2V_2$

$\Rightarrow$ $10^{-6} \times 1 = N_2\left[1 + \dfrac{7}{3}\right]$ $\Rightarrow$ $10^{-6} = N_2 \times \dfrac{10}{3}$

$N_2 = \dfrac{3}{10} \times 10^{-6}$ $\Rightarrow$ $N_2 = 3 \times 10^{-7}$

$[\mathrm{H^+}] < 10^{-6}$

So $[\mathrm{H^+}]$ of water is also added. As common ion effect on H_2O is neglected. So,

$[\mathrm{H^+}] = 3 \times 10^{-7} + 10^{-7} = 4 \times 10^{-7}$ M

$\Rightarrow$ pH = 7 – log 4 = 7 – 0.60 = 6.4

5. (a)
$$\begin{array}{ccccc} \mathrm{HA} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{A^-} \\ \mathrm{C} & & 0 & & 0 \\ \mathrm{C - C\alpha} & & \mathrm{C\alpha} & & \mathrm{C\alpha} \end{array}$$

$K_a = \dfrac{\mathrm{C\alpha^2}}{[1 = \alpha]}$ $\alpha << 0.1$ $\Rightarrow$ $K_a = \mathrm{C\alpha^2}$

pH = 4.52

$[H^+] = \text{Antilog}(-4.52) = \text{Antilog}(-0.48) \times 10^{-5} = 3 \times 10^{-5}$

$\Rightarrow \quad C\alpha = 3 \times 10^{-5} \qquad \Rightarrow \quad \alpha = 3 \times 10^{-4}$

$K_a = 0.1\,[3 \times 10^{-4}]^2 = 9 \times 10^{-9}$

(b) $pH = 10.48$

$pOH = 3.52$

$[OH^-] = \text{Antilog}(-3.52) = \text{Antilog}(1 - 0.48) \times 10^{-4} = 3 \times 10^{-4}$

BOH	$\rightleftharpoons$ B^+	+ OH^-
C	0	0
$C - C\alpha$	$C\alpha$	$C\alpha$

$[OH^-] = C\alpha = 3 \times 10^{-4} \qquad \Rightarrow \quad \alpha = 3 \times 10^{-3}$

$\alpha << 0.1, \quad K_b = C\alpha^2 = 0.1(3 \times 10^{-3})^2 = 9 \times 10^{-7}$

6.

	HCl	H_2SO_4	NaOH
milli mole	20	40	$\frac{2}{40} \times 1000 = 50$
milli eq.	20	80	50

Remaining milli eq. of Acid = 50

$[H^+] = \dfrac{50 \times 10^{-3}}{5} = 10^{-2}\,M \quad \Rightarrow \quad pH_1 = 2$

Now Total milli eq. of Acid = $(50 + 10 \times 2) = 70$

milli eq. of NaOH = $\dfrac{4 \times 10^3}{40} = 100$

As milli eq. of base is greater than milli eq. of acid. So resulting solution is basic. Remaining milli eq. of base = 30

$[OH^-] = \dfrac{30 \times 10^3}{5} = 6 \times 10^{-3}\,M$

$pOH = 3 - \log 6 = 2.22 \quad \Rightarrow \quad pH_2 = 11.78$

So charge in pH = 11.78 − 2 = 9.78

Single Correct Answer Type

7. (a) $[OH^-] = \sqrt{K_w}$ in pure water.

So as temperature increases K_w decreases ⇒ $[OH^-]$ decreases.

8. (b) $[H^+] = \dfrac{50 \times 10^{-1} + 50 \times 10^{-2}}{100} = 5.5 \times 10^{-2}\,M$

$\therefore pH = 2 - 0.74 = 1.26$

9. (d)

(a) HCl — NaOH

No. of milli eq. = $\dfrac{1}{10} \times 100 = 10$ — $\dfrac{1}{10} \times 100 = 10$

So solution is neutral.

(b) $\dfrac{1}{10} \times 55 = 5.5$ — $\dfrac{1}{10} \times 45 = 4.5$

$[H^+] = \dfrac{1}{100} = 10^{-2}\,M, \; pH = 2$

(c) $\dfrac{1}{10} \times 10 = 1$ — $\dfrac{1}{10} \times 90 = 9$ Basic

(d) $\dfrac{1}{5} \times 75 = 15$ — $\dfrac{1}{5} \times 25 = 5$

$[H^+] = 0.1\,M, \; pH = 1$

10. (c) As $V \to \infty$, effect of water dominates. So, pH becomes 7.

11. (d) The value of $[H^+] = [OH^-] = 10^{-7}\,M$ is true only at 25°C.

12. (b) $pH = 13$

$\therefore \quad [H^+] = 10^{-13}\,M$

$[OH^-] = 10^{-1}\,M = 0.1\,mol\,L^{-1}$

$[Ba(OH)_2] = 0.1\,N$

$= 0.1 \times 100 = 10$ milliequivalents

13. (a)

	pH before	pH after	changes
(a)	2	4	2
(b)	12	13.04	1.04
(c)	6	6.7	0.7
(d)	2	7	5

Explanation (a) $pH = 2$, $[H^+] = 10^{-2}\,M$

$M_1V_1 = M_2V_2$

$10^{-2} \times 1 = M_2 \times 100$

$M_2 = 10^{-4}$

$\therefore \; pH = 4$

(b) $[OH^-] = 10^{-2}$

$pOH = 2$

$pH = 12$

100 mL of 0.01 M NaOH contains = 0.001 mol

NaOH added = 0.01 mol

Total moles = 0.011 mol

$\therefore \; [OH^-]_{final} = 0.011 \times 10 = 0.11\,M$

$pOH = 0.96$

$pH = 13.04$

(c) $[HCl] = 10^{-6}\,M$

$[H^+] = 10^{-6}\,M$

$pH = 6$

after dilution $[HCl] = 10^{-7}\,M = [H^+]$

$[H^+]$ in $H_2O = 10^{-7}\,M$

Total $[H^+] = 10^{-7} + 10^{-7} = 2 \times 10^{-7}$

$\therefore \; pH = 7 - \log 2 = 6.74$

(d) $pH = 2$, $[H^+] = 10^{-2}\,M$

$pH = 12$, $[H^+] = 10^{-2}\,M$

$\therefore \; [OH^-] = 10^{-2}\,M$

Thus, on mixing solution becomes neutral, thus pH = 7.

Multiple Correct Answers Type

14. (a, d)

(a) $[H^+] = 10^{-2}$ and $[OH^-] = 10^{-2}$

$H^+ + OH^- \rightarrow H_2O$

This leads complete neutralisation.

So, $\quad pH = 7 = \dfrac{2 + 12}{2}$

(d) $[H^+] = 10^{-5}$ and $[OH^-] = 10^{-2}$

$H^+ + OH^- \rightarrow H_2O$

This leads to complete neutralisation.

So, $\quad pH = 7 = \dfrac{5 + 9}{2}$

15. (a, b)

Total $[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$

$$= \sqrt{\left(3.6 \times 10^{-4} \times \frac{0.5}{500} \times 100\right) + \left(8 \times 10^{-4} \times \frac{0.1}{500} \times 100\right)}$$

$\therefore \quad [H^+] = 10^{-2}$ M.

For HN_3,

$$[N_3^-] = \frac{K_a[HN_3]}{[H^+]} = \frac{3.6 \times 10^{-4} \times 0.5}{0.01 \times 500} \times 100 = 3.6 \times 10^{-3}\,M$$

For HOCN,

$$[OCN^-] = \frac{K_a[HOCN]}{[H^+]} = \frac{8 \times 10^{-4} \times 0.1 \times 400}{0.01 \times 500} = 6.4 \times 10^{-3}\,M.$$

16. (b, c)
On the basis of Ostwald dilution law, number of H^+ ions will increase but increase in volume will be more. Therefore, $[H^+]$ decreases, pH increases.

17. (a, c)
Larger the temperature, larger the ionization of water yielding $[H^+] > 10^{-7}$ mol dm^{-3} and thus pH < 7.

18. (a, c, d)
In 0.6 m M HCOOH solution,

$$K_a = \frac{[H^+]^2}{C - [H^+]} \Rightarrow 8 \times 10^{-4} = \frac{[H^+]^2}{6 \times 10^{-4} - [H^+]}$$

$\therefore \quad [H^+] = 4 \times 10^{-4}$ M.

Matching Column Type

19. (a→p, q, r, s), (b→p, r), (c→r), (d→p, q, s)

(a) $[H^+]$ in HCl solution = 10^{-5} M

$[H^+]$ in H_2S solution = $\sqrt{K_a \times C} = 10^{-4}$ M

So $[H^+]$ in HCl solution < $[H^+]$ in H_2S solution

and $[OH^-]$ in HCl solution > $[OH^-]$ in H_2S solution

and degree of dissociation of water in HCl solution > degree of dissociation of water in H_2S solution

pH of HCl solution > pH of H_2S solution.

(b) At pH = 4.74 in CH_3COOH solution, $[CH_3COO^-] = [CH_3COOH]$

$\therefore$ degree of dissociation of $CH_3COOH = \frac{1}{2}$

At pH = 9.26 i.e. pOH = 4.74 in NH_4OH solution, $[NH_4^+] = [NH_4OH]$

$\therefore$ degree of dissociation of CH_3COOH = degree of dissociation of NH_4OH

degree of dissociation of CH_3COOH solution > degree of dissociation of water in NH_4OH solution.

(c) $[H^+]$ in CH_3COOH solution $= \sqrt{1.8 \times 10^{-5} \times 0.1}$

$= \sqrt{1.8} \times 10^{3}$ M

$[H^+]$ in HCOOH solution $= \sqrt{1.8 \times 10^{-4} \times 1} = \sqrt{1.8} \times 10^{-2}$ M

So, degree of dissociation of CH_3COOH = degree dissociation of HCOOH.

(d) $[H^+]$ in HA_1 solution $= \sqrt{10^{-5} \times 0.1} = 10^{-3}$ M

$[H^+]$ in HA_2 solution $= \sqrt{10^{-6} \times 0.1} = 10^{-4}$ M

So, $[OH^-]$ in solution of HA_1 < $[OH^-]$ in solution of HA_2

pH in solution of HA_1 < pH in solution of HA_2

and degree of dissociation of water HA_1 < degree of dissociation of water HA_2.

Comprehension Type

20. (a) $C = 10^{-6}$

$K_a = 1.8 \times 10^{-5}$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{10^{-6}}} = \sqrt{18} = 4.24$$

$\therefore \alpha = 4.24$

$[H^+] = C\alpha = 10^{-6} \times 4.24$

21. (d) $H_2S \rightleftharpoons H^+ + HS^-$; $\quad K_{a1}$

$HS^- \rightleftharpoons H^+ + S^{2-}$; $\quad K_{a2}$

pH = 3

$\therefore [H^+] = 0.001; \quad [H_2S] = 0.1$

$$K_{a1} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$K_{a2} = \frac{[H^+][S^{2-}]}{[H_2S]}$$

$$K_{a1} \times K_{a2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$\Rightarrow \quad [S^{2-}] = \frac{K_{a1} \times K_{a2} \times [H_2S]}{[H^+]^2}$$

$$= \frac{10^{-7} \times 1.3 \times 10^{-13} \times 0.1}{(0.001)^2} = 1.3 \times 10^{-15}.$$

22. (a) $C = 0.01$ M, $K_a = 1.4 \times 10^{-4}$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-4}}{10^{-2}}} = \sqrt{1.4 \times 10^{-2}}$$

$\alpha = 0.118$

$[H+] = C\alpha = 0.01 \times 0.118 = 0.00118$

$pH = -\log [H^+] = 2.926$

DPP 7.3

Subjective Type

1. $C_5H_5NH^+Cl^-$ It is salt of SAWB.

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

$$\Rightarrow \quad pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log 0.25$$

$\Rightarrow \quad pK_b = 9.1$

$K_b = \text{Antilog}(-9.1) = 8 \times 10^{-10}$

2. $pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

$K_a = 1.6 \times 10^{-5}$ and $K_b = 1.6 \times 10^{-5}$

$$\therefore pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b = 7$$

Now degree of hydrolysis $= h = \sqrt{\dfrac{K_w}{K_aK_b}} = 6.25 \times 10^{-3}$

% hydrolysis = 0.625%

3. $CrO_4^- + H_2O(l) \rightleftharpoons HrCO_4^- + OH^-$

$$K_h = \frac{K_w}{K_a} = 2 \times 10^{-8} \quad \text{and} \quad K_h = Ch^2 = 2 \times 10^{-8}$$

$$\Rightarrow \quad h^2 = \frac{2 \times 10^{-8}}{0.005} \qquad \therefore h = 2 \times 10^{-3}$$

4. $NaHCO_3 \qquad [C] = 0.1$ M

$$pH = \frac{pK_1 + pK_2}{2} = \frac{7 - \log 4.5 + 11 - \log 4.5}{2}$$

$$= \frac{18 - 2\log 4.5}{2} = 9 - \log 4.5 = 9 - 0.66 = 8.34$$

5. $\underset{\text{Weak}}{HA} + \underset{\text{Strong}}{BOH} \rightleftharpoons BA + H_2O$

$HA + B^+ + OH^- \rightleftharpoons B^+ + A^- + H_2O$

or $HA + OH^- \rightleftharpoons A^- + H_2O$

$$K_h = \frac{[A^-]}{[HA][OH^-]}$$

In the above reaction,

$$K_h = \frac{[HA][OH^-]}{[A^-]}$$

So, $K = \frac{1}{K_h}$

We know that, $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.0 \times 10^{-4}} = 10^{-10}$

$$K = \frac{1}{10^{-10}} = 10^{10}$$

Single Correct Answer Type

6. (a) NaCN and NaOBr, It is a fact.

7. (d) K_2CO_3 It is a fact.

8. (a) $h = 0.03$

$K_h = Ch^2 = 9 \times 10^{-5}$

$$K_h = \frac{K_w}{K_a} = 9 \times 10^{-5}$$

$$\Rightarrow K_a = \frac{10^{-14}}{9 \times 10^{-5}} = 1.11 \times 10^{-10} \approx 1 \times 10^{-10}$$

9. (b) For Na_2HPO_4, $pH = \frac{pK_{a_2} + pK_{a_3}}{2} = \frac{7.28 + 12}{2} = 9.6$

For Na_2HPO_4, $pH = \frac{pK_{a_1} + pK_{a_3}}{2} = \frac{2.2 + 7.2}{2} = 4.7$

10. (b) Solution of HCl and NH_4Cl will be acidic, solution of NaCl neutral whereas solution of NaCN will be basic.

11. (a) pH of amphiprotic salts and weak acid-weak base salt is independent of its concentration.

12. (b) Volume of (2/15) M HCl to neutralize the given 2.5 mL of (2/5) M weak monoacidic base is

$$V_{acid} = \frac{V_{base} M_{base}}{M_{acid}} = \frac{(2.5\text{mL})\{(2/5)\text{M}\}}{\{(2/15)\text{M}\}} = 7.5 \text{ mL}$$

Total volume of solution at the equilibrium point = 2.5 mL + 7.5 mL = 10.0 mL

Molarity of the salt (B^+Cl^-) at the equivalence point is

$$M_{salt} = \frac{V_{base} M_{base}}{V_{total}} = \frac{(2.5 \text{ mL})\{(2/5)\text{M}\}}{(10 \text{ mL})} = 0.1 \text{ M}$$

The cation of the salt formed undergoes hydrolysis $B^+ + H_2O \rightleftharpoons BOH + H^+$, the hydrolysis constant of this reaction is

$$K_h = \frac{[BOH]}{[B^+][OH^-]}$$

Multiplying and dividing by $[OH^-]$ in the solution, we get

$$K_h = \frac{[BOH]}{[B^+][OH^-]}[H^+][OH^-] = \frac{K_w}{K_b} \frac{10^{-14}\text{M}^2}{10^{-12}\text{M}} = 10^{-2}\text{M}$$

13. (b) $K_h = \frac{K_w}{K_a K_b} = \frac{1.0 \times 10^{-14}}{(1.8 \times 10^{-5}\text{M})(4.6 \times 10^{-10}\text{M})} = 1.21$

14. (b) Hydrolysis constant $K_h = \frac{1}{K_{eq}} = 10^{-9}$

$$[OH^-] = \sqrt{CK_h} = \sqrt{0.1 \times 10^{-9}} = 10^{-5} \text{ M}$$

pOH = 5, pH = 9

15. (c) $K_a(HA) = \frac{K_w}{K_h} = \frac{10^{-14}}{10^{-8}} = 10^{-6}$

$$K_a(HB) = \frac{K_w}{K_h} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

$K_a(HC) = 10^{-2}$

Greater the value of dissociation constant K_a, more is the acidic strength.

Multiple Correct Answers Type

16. (b, c)

(a) $K_a(HCN) < K_a(CH_3COOH)$. Since $K_h = K_w/K_a$, K_h for CN^- ions is larger than CH_3COO^- ions.

(d) The solution of NH_4CN is alkaline and CN^- undergoes more hydrolysis than NH_4OH.

17. (a, b)

Salts of strong acid and strong base do not undergo hydrolysis.

18. (b, c)

$H_2SO_4^-$ can accept H^+ only whereas H_3PO_4 can give up H^+ only.

Matching Column Type

19. (a→q, s), (b→p, r), (c→p, r, q), (d→q, s)

Cationic Hydrolysis : Salts of strong acids and weak bases give acidic solutions in water.

E.g.: $CuSO_4$ solution, Potash alum solution.

Let BA be one of such salts. When it is put into water, the reaction is as follows :

$B^+ + A^- + H_2O \rightleftharpoons BOH(aq) + H^+(aq) + A^-(aq)$

The net reaction of hydrolysis is :

$B^+ + A^- + H_2O \rightleftharpoons BOH(aq) + H^+(aq)$

Anionic Hydrolysis ; Salts of weak acids and strong bases give alkaline solutions in water.

E.g.: $NaHCO_3$ NaCN etc.

Let BA represents such a salt. As put in water,

$$BA(aq) + H_2O(aq) \rightleftharpoons BOH(aq) + HA(aq)$$

BA dissociates into ions and BOH being strong base also ionises.

$$B^+ + A^- + H_2O \rightleftharpoons B^+(aq) + \bar{O}H + HA(aq)$$

So, the net solution is

$$A^-_{(aq)} + H_2O \rightleftharpoons \bar{O}H(aq) + HA(aq)$$

Integer Type

20. (5)

$$\begin{array}{llll} & C_6H_5NH_2 & + \; H^+ & \rightarrow C_6H_5NH_3^+ \\ t=0 & 5 & 2.5 & \\ t_{eq} & 2.5 & — & 2.5 \end{array}$$

$pOH = pK_a = 14 - 8 = 6$

$\therefore pK_a = 6$

$$pH = 7 - \frac{1}{2}pK_a - \frac{1}{2}\log C = 7 - \frac{6}{2} - \frac{1}{2}\log(0.01) = 5$$

21. (6) $Zn^2 + H_2O \rightleftharpoons Zn(OH)^+ + H^+$

$K_h = 1 \times 10^{-9}$

$$K_h = \frac{K_w}{K_b\,(Zn(OH)_2}$$

$$\therefore \quad K_b = \frac{K_w}{K_h} = 1 \times 10^{-5}$$

$pK_b = 5$

$$\therefore \quad pH = 7 - \left(\frac{pK_b + \log C}{2}\right) = 7 - \frac{(5-3)}{2} = 6$$

Comprehension Type

22. (d) It is a fact.

23. (a) Since K_a of CH_3COOH and K_b of NH_4OH are same. So degree of hydrolysis of CH_3COO^- and NH_4^+ are exactly same.

24. (c) It is a fact.

DPP 7.4

Subjective Type

1. (a) $CH_3COOH = 0.2$ M

$$[H^+] = \sqrt{K_a \times C} = \sqrt{2 \times 10^{-5} \times 0.2} = \sqrt{4 \times 10^{-6}} = 2 \times 10^{-3}$$

$$C\alpha = [H^+] \quad \Rightarrow \quad \alpha = \frac{2 \times 10^{-3}}{2 \times 10^{-1}} \quad \Rightarrow \quad \alpha = 0.01$$

(b)

$$\begin{array}{lll} HCl \rightarrow & H^+ \; + & Cl^- \\ 0.1 & 0.1 & 0.1 \end{array}$$

$[H^+] = 0.1 \qquad pH = 1$

$$\begin{array}{lll} CH_3COOH \rightleftharpoons & CH_3COO^- \; + & H^+ \\ 0.2 & 0 & 0.1 \\ 0.2\,(1-\alpha) & 0.2\alpha & 0.1 + 0.2\alpha = 0.1\alpha \end{array}$$

$$K_a = \frac{0.2\alpha \times 0.1}{0.2} = 2 \times 10^{-5} \quad \Rightarrow \alpha = 2 \times 10^{-4}$$

(c) $[CH_3COO^-] = 0.2 \times 2 \times 10^{-4} = 4 \times 10^{-5}$

(d) % change in α

$$= \frac{1 \times 10^{-2} - 2 \times 10^{-4}}{1 \times 10^{-2}} \times 100 = \left[1 - \frac{2}{100}\right] \times 100 = 98\%$$

2. (a)

$$Ag_3PO_4(s) \rightleftharpoons \underset{3s}{3Ag^+_{(aq)}} + \underset{s}{PO_4^{3-}(aq)}$$

$K_{sp} = 27(s)^4 = 2.7 \times 10^{-23} \Rightarrow s = 10^{-6}$ mole/lit

$= 419 \times 10^{-6}$ gram/lit

$= 4.19 \times 10^{-4}$ gram/lit

(b)

$$\begin{array}{lll} AgNO_3 \rightleftharpoons & Ag^+ \; + & NO_3^- \\ & 0.02 & 0.02 \end{array}$$

$$Ag_3PO_4 \rightleftharpoons 3Ag^+ + PO_4^{3-}$$

$3x + 0.02$

≈ 0.02

$K_{sp} = (0.02)^3\,(x) = 2.7 \times 10^{-23}$

$$\Rightarrow x = \frac{27}{8} \times 10^{-18} = 3.375 \times 10^{-18} \text{ mole/lit}$$

$= 3.375 \times 10^{-18} \times 419$ gram/lit

$= 1.414 \times 10^{-15}$ gram/lit

3.

$$\begin{array}{lll} SrSO_4 \rightleftharpoons & Sr^{+2} \; + & SO_4^{-2} \\ & x & (x+y) \end{array} \qquad \begin{array}{lll} BaSO_4 \rightleftharpoons & Ba^{+2} \; + & SO_4^{-2} \\ & y & (x+y) \end{array}$$

$K_{sp}\,(BaSO_4) = y(x + y)$

$K_{sp}\,(SrSO_4) = x(x + y)$

$$\frac{K_{sp}(SrSO_4)}{K_{sp}(BaSO_4)} = \frac{x}{y} = \frac{7.5}{0.6} = 12.5 \qquad \Rightarrow x = 12.5y$$

$y[12.5y + y] = 6 \times 10^{-8} \qquad 13.5y^2 = 6 \times 10^{-8}$

$$y^2 = \frac{600}{13.5} \times 10^{-10} = 44.4 \times 10^{-10} \qquad \Rightarrow y = 6.67 \times 10^{-5}\text{ N}$$

$x = 8.33 \times 10^{-4}$ M

$(x + y) = 9 \times 10^{-4}$ M

4. Let V mL of each is mixed.

$$[Cu^{+2}] = \frac{0.002 \times V}{2V} = 0.001 \quad \text{and} \quad [IO_3^-] = \frac{0.002 \times V}{2V} = 0.001$$

$K_{sp} = (0.001)(0.001)^2 = 10^{-3} \times 10^{-6} = 10^{-9}$

$K_{IP} < K_{sp} \rightarrow$ No ppt. formation

5. (a) $Hg\,(CN)_2 \rightarrow Hg^{+2} + 2CN^-$

$K_{sp} = 4s^3 = 1.35 \times 10^{-23} \Rightarrow s = 1.5 \times 10^{-8}$ M

(b) Miligram of $Hg(CN)_2 = [1.5 \times 10^{-8}] \times 252 \times 10^3$

$= 3.78 \times 10^{-3}$ mg/lit

(c) $\therefore 3.78 \times 10^{-6}$ are dissolved in 1 litre

$$\therefore 1.134 \text{ gram are dissolved in} = \frac{1 \times 1.134}{3.78 \times 10^{-6}}\text{ lt} = \frac{11.34 \times 10^5}{3.78}\text{ lt}$$

$= 3 \times 10^5$ lt $= 3 \times 10^8$ mL

6. Let solubility of CaC_2O_4 is s mole/lit.

$$CaC_2O_4\,(s) \rightleftharpoons \underset{s}{Ca^{+2}\,(aq)} + \underset{s}{C_2O_4^{2-}\,(aq)}$$

$C_2O_4^{2-}$ react with H^+ to produce $HC_2O_4^-$ and $H_2C_2O_4$.

$$H^+ + C_2O_4^{2-} \rightleftharpoons HC_2O_4^- \; ; \quad K_1' = \frac{1}{K_2}$$

$$\frac{1}{K_2} = \frac{[HC_2O_4^-]}{[H^+][C_2O_4^{2-}]} \quad \Rightarrow \quad [H_2C_2O_4^-] = \frac{[H^+][C_2O_4^{2-}]}{K_2}$$

Again this $HC_2O_4^-$ react with H^+ as:

$$HC_2O_4^- + H^+ \rightleftharpoons H_2C_2O_4;\ K_1' = \frac{1}{K_1}$$

$$\frac{1}{K_1} = \frac{[H_2C_2O_4]}{[HC_2O_4^-][H^+]} \Rightarrow [H_2C_2O_4] = \frac{[HC_2O_4^-][H^+]}{K_1}$$

Putting the value of $[HC_2O_4^-] + [H_2C_2O_4] = s$

$$[C_2O_4^{2-}]\left[1 + \frac{[H^+]^+}{K_2} + \frac{[H^+]^2}{K_1K_2}\right] = s$$

$$[C_2O_4^{2-}]\left[1 + \frac{10^{-4}}{5\times10^{-5}} + \frac{10^{-8}}{25\times10^{-7}}\right] = s$$

$$[C_2O_4^{2-}] = \left(\frac{s}{3}\right) \Rightarrow K_{sp} = [Ca^{+2}]\,[C_2O_4^{2-}] = 2.7\times10^{-9}$$

$$\frac{s^2}{3} = 2.7\times10^{-9} \Rightarrow s = 9\times10^{-5}\,M$$

7. $Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2(s)$

10×10^{-3} mol 20×10^{-3} mol —

— — 10×10^{-3} mol

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$

s $2s$

where s is the solubility of $Mg(OH)_2$ in the resulting solution.

$\therefore\ 4s^3 = 12\times10^{-12}$

$\therefore\ s = (3)^{1/3}\times(10^{-12})^{1/3} = 1.44\times10^{-4}$ (M)

$\therefore\ [OH^-] = 2s = 2.88\times10^{-4}$ (M)

or $pOH = 4 - \log 2.88 = 4 - 0.459 = 2.541$

$\therefore\ pH = 14 - pOH = 14 - 2.541 = 11.459$

Single Correct Answer Type

8. (c) $CaF_2(s) \rightleftharpoons Ca^{2+} + 2F^-$

s $2s$

$4s^3 = K_{sp} = 4\times10^{-11} \Rightarrow s = 2.15\times10^{-4}$ M

So, amount of F^- in 20000 L of water $= 2s\times20000 = 8.6$ mol.

9. (a) $S^{2-} + Zn^{2+} \rightarrow ZnS(s)$

m. moles 0.4 0.2

0.2 —

So in solution,

$$[S^{2-}] = \frac{0.2}{20} = 0.01\,M$$

$$\therefore\ [Zn^{2+}] = \frac{K_{sp}}{[S^{2-}]} = \frac{4\times10^{-24}}{0.01} = 4\times10^{-22}\,M$$

$\therefore$ Mass of Zn^{2+} remain unprecipitated in 20 mL of solution

$$= \frac{4\times10^{-24}}{1000}\times20\times65 = 5.2\times10^{-22}\,g$$

10. (d) (a) $Li_3Na_3(AlF_6)_2 \rightarrow 3Li^+ + 3Na^+ + 2[AlF_6]^{3-}$

3s 3s 2s

$K_{sp} = (3s)^3(3s)^3(2s^2) = 2916\,s^8$.

11. (b) K_{sp} of $Mg(OH)_2 = 2.56\times10^{-13}$

$4s_1^3 = 2.56\times10^{-13} \Rightarrow s_1 = 4\times10^{-5}$ M

K_{sp} of Al $(OH)_3 = K_{sp} = 4.32\times10^{-34}$

$27s_2^4 = 4.32\times10^{-34} \Rightarrow s_2 = 2\times10^{-9}$ M

$$\frac{s_1}{s_2} = \frac{4\times10^{-5}}{2\times10^{-9}} = 2\times10^4$$

12. (c) $NaF \rightarrow Na^+ + F^-$

0.1 0.1 0.1

$CaF_2 \rightarrow Ca^{2+} + 2F^-$

$(2x + 0.1) \approx 0.1$

$K_{sp} = x(0.1)^2 = 3.4\times10^{-11} \Rightarrow x = 3.4\times10^{-9}$

13. (a) For choice (a), the ionic-product exceeds solubility product.

$[Ag^+][Cl^-] = (10^{-4}\,M)(10^{-4}\,M) = 10^{-8}\,M^2$

14. (b) $s_0 = \sqrt{K_{sp}(AgCl)}$; $s_1 = K_{sp}(AgCl)/0.02\,M$; $s_2 = K_{sp}(AgCl)/0.01\,M$;

$s_3 = K_{sp}(AgCl)/0.05\,M$

Hence, $s_0 > s_2 > s_1 > s_3$.

15. (b) On mixing the two solutions, 0.1 M of $AgNO_3$ which is left in excess becomes 0.05 M due to doubling of the volume. Hence

$$[Cl^-] = \frac{K_{sp}(AgCl)}{[Ag^+]} = \frac{1.8\times10^{-10}\,M^2}{0.05\,M} = 3.6\times10^{-9}\,M$$

16. (a) $K_{sp}(BaCrO_4) = 2.4\times10^{-10}\,M^2$

$[CrO_4^{-2}] = 6\times10^{-4}$

$K_{sp}(BaCrO_4) = [Ba^{+2}][CrO_4^{-2}] = 2.4\times10^{-10}$

$\Rightarrow [Ba^+]\times6\times10^{-4} = 2.4\times10^{-10}$

$[Ba^+] = 4\times10^{-7}$ M

17. (a) $pH = 4 \Rightarrow [H^+] = 10^{-4}\,M \Rightarrow [OH^-] = 10^{-10}\,M$

$Al(OH)_3 \rightleftharpoons Al^{+3} + 3OH^-$

$K_{sp}(Al(OH)_3) = [Al^{+3}] + [OH^-]^3$

$[Al^{3+}][OH^-]^3 = 1\times10^{-33}$

$[Al^{3+}](10^{-10})^3 = 1\times10^{-33} \Rightarrow [Al^{3+}] = 10^{-3}$ M

18. (a) **Order of solubility:** Complex formation > Pure water > Common ion effect.

AgBr form complex $[Ag(NH_3)_2]^+$ in NHs_3. So, solubility is maximum in NH_3 (aq).

Multiple Correct Answers Type

19. (c, d)

In $AgNO_3$ solution, the solubility of AgCN will decrease as compared to pure water because of common ion effect of Ag^+ ion.

In NH_3 solution and buffer of pH = 5, the solubility of AgCN will increase due to complex formation in case of NH_3 solution and hydrolysis of CN^- ions in case of buffer of pH = 5.

20. (a, b)

$K_{sp} = 1.1\times10^{-11} = (1.4\times10^{-4})^{x+y}\,x^x \,.\, y^y$

So we have $x + y = 3$ (by comparing values).

$$\text{so,}\quad x^x\cdot y^y = \frac{1.1\times10^{-11}}{1.4\times1.4\times1.4\times10^{-12}} = \frac{110}{1.96\times1.4} = 4$$

Hence $x = 1$, $y = 2$ or

$y = 1$, $x = 2$

21. (c, d)

$CaF_2 \rightarrow Ca^{2+} + 2F^-$

(solubility) S S 2S

$\therefore\ 2[Ca^{2+}] = [F^-]$

$K_{sp} = [Ca^{2+}] = [F^-]^2 = S\times[2S]^2 = 4S^3$

$$S = \left[\frac{K_{sp}}{4}\right]^{1/3};\ [Ca^{2+}] = \left[\frac{K_{sp}}{4}\right]^{1/3}$$

22. (a, b, c, d)

$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+} + 3PO_4^{3-}$

3s 2s

$\therefore \quad K_{sp} = 2.05 \times 10^{-33} = 108s^5$

$\therefore \quad s = 1.63 \times 10^{-6}$ M

$\therefore \quad [Ca^{2+}] = 3 \times 1.63 \times 10^{-6} = 4.9 \times 10^{-6}$ M

$[PO_4^{3-}] = 2 \times 1.63 \times 10^{-6} = 3.26 \times 10^{-6}$ M

$[CaPO_4]_{eq} = 0$, because all the salt is in ionic state.

23. (d) pOH of $Ba(OH)_2 = 2$

$\therefore [OH^-] = 10^{-2}$ M; $[Ba^{2+}] = 0.5 \times 10^{-2}$ M

$K_{sp} = [Ba^{2+}][OH^-]^2$

$= 0.5 \times 10^{-2} \times [10^{-2}]^2$

$= 5 \times 10^{-7}$ M^3

Matching Column Type

24. (a→s), (b→p, q), (c→q, s), (d→q, r)

(a) For AgBr, $K_{sp} = [Ag^+][Br^-]$

So on increase in $[Br^-]$, solubility of AgBr decreases.

(b) For AgCN, $K_{sp} = [Ag^+][CN^-]$

CN^- undergoes hydrolysis, so solubility in water is more than expectation.

In acidic solution, CN^- gets protonated. So, solubility of AgCN increases.

AgCN forms complex $Ag(CN)_2^-$ with excess of CN^-.

(c) For $Fe(OH)_3$, $K_{sp} = [Fe^{3+}][OH^-]^3$.

In acidic solution OH^- decreases, so solubility increases.

Solubility decreases in presence of OH^-.

(d) For $Zn(OH)_2$, $K_{sp} = [Zn^{2+}][OH^-]^2$

$Zn(OH)_2$ is amphoteric in nature, so its solubility increases in both acidic as well as strongly basic solution.

Integer Type

25. (1) $Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$

$2 \times 0.01 \quad 0.01$

$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$

$(x + 0.01) \approx 0.01$

$K_{sp} = 4x^2(0.01)$

$K_{sp} = 4s^3 = 4 \times 10^{-12} = 4x^2(0.01) \quad \Rightarrow \quad x = 10^{-5}$

26. (2) $M[OH]_x \rightleftharpoons M^{x+} + xOH^-$

$\therefore \quad (S)(xS)^x = K_{sp}$

$x^xS^{x+1} = 4 \times 10^{-12}$

$x^x(10^{-4})^{x+1} = 4 \times 10^{-12}$

$\therefore \quad x = 2$

Comprehension Type

27. (a) For SrF_2 in pure water

$4s_1^3 = K_{sp}$

For SrF_2 in 0.1 M NaF solution

$\Rightarrow \quad 4s_1^3 = s_2\,(0.01)$

$\Rightarrow \quad 4s_1^3 = s_1 \times \frac{256}{10^6}(0.01$

$\Rightarrow \quad s_1 = 8 \times 10^{-4}$ M

$\therefore \quad K_{sp} = 4s_1^3 = 2.048 \times 10^{-9}$

28. (c) $[Sr^{2+}]_i = 0.0011 = 11 \times 10^{-4}$ M

$[Sr^{2+}]_f = 2 \times 10^{-4}$ M

$\therefore \quad [Sr^{2+}]$ precipitated $= (11 - 2) \times 10^{-4}$ M

$= 9 \times 10^{-4}$ M

$[F^-]$ needed for this precipitation $= 2 \times 9 \times 10^{-4} = 18 \times 10^{-4}$ M

Also, $[Sr^{2+}]_f\,[F^-]_f^2 = K_{sp} = 2.048 \times 10^{-9}$

But, $[Sr^{2+}]_f = 2 \times 10^{-4}$ M

$\therefore \quad [F^-]_f = 3.2 \times 10^{-3}$ M

$\therefore$ Total $[F^-]$ needed $= 3.2 \times 10^{-3} + 18 \times 10^{-4} = 5 \times 10^{-3}$ M

$\therefore$ NaF needed for 100 mL solution $= \frac{5 \times 10^{-3} \times 42}{10} = 0.021$ g

29. (b) $SrF_2 \rightarrow Sr^{2+} + 2F^-$

s 2s

F^- will react with H^+ to produce HF.

$F^- + H^+ \rightleftharpoons HF$

$$K = \frac{1}{K_a} = \frac{[HF]}{[H^+][F^-]} = \frac{7}{10^{-5}}$$

$\therefore \quad [HF] = 7 \times 10^5\,[F^-][H^+] \qquad (\because [H^+] = 10^{-5};\ pH = 5)$

$= 7 \times 10^5\,[F^-] \times 10^{-5} = 7\,[F^-]$

Here $[F^-] + [HF] = 2s$

$\therefore \quad [F^-] = \frac{s}{4}$

$$K_{sp} = s\left(\frac{s}{4}\right)^2 = 2.048 \times 10^{-9}$$

$\therefore \quad s = 3.2 \times 10^{-3}$ mol/L

DPP 7.5

Subjective Type

1. $pOH = -\log K_b + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]}$

or $\quad pOH = -\log K_b + \log \frac{[NH_4^+]}{[NH_4OH]}$

$\because \quad [NH_4^+] = \frac{a}{500}; \qquad [NH_4OH] = \frac{100}{500}$

$4.65 = -\log 1.78 \times 10^{-5} + \log \frac{a/500}{100/500}$

$4.65 = 4.7496 + \log \frac{a}{100} \qquad \therefore \quad a = 79.51$

$\therefore \quad$ Millimole of $(NH_4)_2\,SO_4$ added $= \frac{a}{2} = \frac{79.51}{2} = 39.775$

$\therefore \quad \frac{w}{132} \times 1000 = 39.775 \quad \therefore \quad w(NH_4)_2SO_4 = 5.248$ g

2. **Case I:**

	BOH + HCl		→	BCl +	H_2O
Millimole before reaction	a	$1.0 \times 5 = 0.5$		0	0
Millimole after reaction	$(a - 0.5)$	0		0.5	0.5

$$\because pH = 10.04 \quad \therefore \quad pOH = -\log K_b + \log \frac{[B^+]}{[BOH]} \qquad (1)$$

$$\therefore pOH = 3.96 \quad \therefore \quad 3.96 = -\log K_b + \log \frac{0.5}{(a-0.5)} \qquad (2)$$

Case II:

	BOH + HCl		→	BCl +	H_2O
Millimole before reaction	a	$0.1 \times 20 = 2$			
Millimole after reaction	$(a - 0.2)$	0		2	2

$$\because pH = 9.14 \quad \therefore \quad pOH = -\log K_b + \log \frac{[B^+]}{[BOH]} \qquad (3)$$

$$\therefore pOH = 4.86 \quad \therefore \quad 4.86 = -\log K_b + \log \frac{2}{(a-2)} \qquad (4)$$

Solving Eqs. (2) and (4), $K_b = 1.81 \times 10^{-5}$

3. For neutralization:

Total Meq. of acid = Meq. of base = $26.6 \times 0.1 = 2.66$

Now for partial neutralization of acid

	HA +	BOH →	BA +	H_2O
Meq. before reaction	2.66	1.2	0	0
Meq. after reaction	1.46	0	1.2	1.2

The resultant mixture acts as a buffer and [HA] and [BA] may be placed in terms of Meq., since volume of mixture is constant.

$$\therefore \quad pH = -\log K_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

or $\quad 5 = -\log K_a + \log \dfrac{[1.2]}{[1.46]}$

$$K_a = 8.219 \times 10^{-6}$$

4. If x is the solubility of $Pb(OH)_2$ in water, we will have

$$\underset{}{Pb(OH)_2(s)} \rightleftharpoons \underset{x}{Pb^{2+}(aq)} + \underset{2x}{2OH^-(aq)}$$

$K_{sp} = [Pb^{2+}][OH^-]^2 = x(2x)^2 = 4x^3$

It is given that $x = 6.7 \times 10^{-6}$ M. Hence,

$K_{sp} = (6.7 \times 10^{-6}\ M)^3 = 1.20 \times 10^{-15}\ M^3$

The solubility of $Pb(OH)_2$ in a buffer solution of pH = 8 (i.e. $[H^+] = 10^{-8}$ M or $[OH^-] = 10^{-6}$ M) will be

$$[Pb^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.20 \times 10^{-15}\ M^3}{(10^{-6}\ M)^2} = 1.20 \times 10^{-3}\ M.$$

5. From definition,

Buffer capacity (ϕ) = $\dfrac{\partial b}{\partial[pH]}$

$\partial[pH] = (4.832 - 4.745) = 0.087;\ \partial b = 0.01$

Substituting given values, $\phi = \dfrac{0.01}{0.087} = 0.115.$

6. On adding HCl, the free hydrogen ions will combine with CH_3COO^- ions to from CH_3COOH. Thus, the concentration of acetic acid increases while that of CH_3COO^- ions decreases.

$[CH_3COOH] = (0.2 + 1) = 1.2$ mol litre^{-1}

[Salt] = $(1 - 0.2) = 0.8$ mol litre^{-1}

Applying Henderson's equation,

$$pH = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$= \frac{0.8}{1.2} - \log 1.8 \times 10^{-5}$$

$$= \log 2 - \log 3 - \log 1.8 \times 1.8^{-5} = 4.5687$$

Single Correct Answer Type

7. (d) Ammonium acetate contains strong conjugate cation and strong conjugate anion. Hence, its solution can be used as a buffer solution.

8. (c) On diluting a buffer solution, the ratio of salt to acid (or base) does not change. Hence, its pH remains constant.

9. (d) We have

	CH_3NH_2 +	HCl	$\longrightarrow CH_3\overset{+}{N}H_3$ +	Cl^-
Initially	0.1 mol	0.08 mol	0	0
Finally	0.02 mol		0.08 mol	0.08 mol

The expression of K_b of CH_3NH_2 is

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

Hence, $\quad K_b = \dfrac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \dfrac{(0.08\ mol)[OH^-]}{0.02\ mol}$

$$[OH^-] = \frac{K_b}{4} = \frac{6 \times 10^{-4}\ M}{4} = 1.5 \times 10^{-4}\ M$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-4}\ M^2}{1.5 \times 10^{-4}\ M} = 6.7 \times 10^{-11}\ M$$

10. (b) We have

$$pH = pK_a^o + \left[\frac{\text{salt}}{\text{acid}}\right] = pK_a^o + \log\left[\frac{n_{salt}}{n_{acid}}\right]$$

$8.5 = 9.2 + \log\left(\dfrac{n_{salt}}{0.05\ mol}\right) = 9.2 + \log(n_{salt}/mol) - \log(0.05)$

$-0.7 = \log(n_{salt}/mol) - (2.6990)$

$\log(n_{salt}/mol) = -2.0$ or $n_{salt} = 10^{-2}$ mol

Since $(NH_4)_2SO_4$ includes $2NH_4^+$ ions, the amount of $(NH_4)_2SO_4$ required will be 0.005 mol.

11. (b) $H_3PO_4 + PO_4^{3-} \longrightarrow H_2PO_4^- + HPO_4^{2-}$

$$[H_2PO_4^-] = [HPO_4^{2-}] \qquad (1)$$

The resultant solution will be a buffer solution.

$$\therefore \quad pH = pK_{a_2} + \log\left[\frac{HPO_4^{2-}}{H_2PO_4^-}\right] \qquad (2)$$

From (1) and (2), $pH = pK_{a_2}$.

Multiple Correct Answers Type

12. (a, c)

Buffer solutions can be obtained by

(i) by mixing a weak acid with its salt with a strong base

(ii) by mixing a weak base with its salt with a strong acid

(iii) by a solution of ampholyte

(iv) by a mixture of an acid salt and a normal salt of a polybasic acid

13. (b, c)

Acidic buffer: $pH = pK_a + \log \frac{[salt]}{[acid]}$. If more salt is added, pH increases.

$pOH = pK_b + \log \frac{[salt]}{[base]}$. If more salt is added, pOH increase and pH decreases.

14. (b, d)

[Borax + Boric acid] → It is buffer because it contains weak acid and salt of weak acid with strong base.

[$NH_4Cl + NH_4OH$] → It is also a buffer because it contains weak base and its salt with strong acid.

15. (b) NaH_2PO_4 is more acidic than Na_2HPO_4, hence NaH_2PO_4 will be considered as acid and Na_2HPO_4 will be considered as salt. In the Henderson Equation, dissociation constant of acid is considered, i.e.,

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$$

So, K_2 is appropriate dissociation constant to be used in Henderson Equation.

16. (a, b)

HPO_4^{2-} is conjugation base of $H_2PO_4^-$.

Matching Column Type

17. (a → q), (b → t), (c → s), (d → p)

(a) Acetic acid + Sodium acetate, forms acidic buffer whose pH lies in the range 3.7 – 5.6.

(b) Borax + Boric acid → It is a buffer because it contains weak acid and salt of weak acid with strong base and pH lies in the range 6.8 – 9.2. Here, instead of donating hydrogen ion, H_3BO_3 actually takes hydroxyl ion from water.

(c) Borax is a weak base and NaOH is a strong base, buffer solution of these two lies in the range 9.2 – 11.0.

(d) The buffer solution of Phthalic acid ($C_6H_4(COOH)_2$) and Potassium acid phthalate ($C_8H_5O_4K$) lies in the range 2.2 – 3.8.

Integer Type

18. (4) $pH = -\log K_a + \log \frac{[\text{Conjugate base}]}{[\text{acid}]} = 10^{-4} + \log \frac{1}{2} = 4$

$[\because pK_a + pK_a = 14]$

19. (5) $pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$$= 4.75 + \log \frac{0.25}{0.125} = 5.05$$

Comprehension Type

20. (b) A weak acid and its conjugate base HPO_4^{2-}.

21. (a) Buffer capacity (ϕ)

$$= \frac{\text{No. of moles of acid or base added to 1 litre}}{\text{Change in pH}}$$

22. (b) For acidic buffer when $\frac{[salt]}{[acid]} = \frac{1}{10}$, then $pH = pK_a - 1$

So, weak acid may be used for preparing buffer solutions having pH values lying within the range $pK_a + 1$ and $pK_a - 1$. The acetic acid has a pK_a of about 4.8, it may, therefore, be used for making buffer solutions with pH values lying roughly within the range 3.8 to 5.8.

23. (b) Buffer capacity is maximum when [salt] = [base]. i.e., $pOH = pK_b$ for base buffer under above condition, the buffer is called efficient.

DPP 7.6

Subjective Type

1. $K_a = 1 \times 10^{-5}$ and $pK_a = 5$

$$pH = pK_{HIn} + \log \left[\frac{\text{ionised}}{\text{unionised}}\right]$$

The dissociation equilibrium for acid indicator

$HIn \rightleftharpoons H^+ + In^-$

Colour A   Colour B

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

The middle point of the colour range of an indicator HIn is the point at which [HIn] = [In].

$pH = pK_{HIn} = 5$

Thus colour change in indicator will be noticed at pH = 5.

(ii) $pH = pK_a + \log \frac{[\text{ionised}]}{[\text{unionised}]} = 5 + \log\left(\frac{80}{20}\right) = 5.6$

2.

	NH_4OH +	$HCl \longrightarrow$	$NH_4Cl + H_2O$
Milimole at mid point	2.25	2.25	2.25

Milimole $= N_1 \times V_{HCl} = 2.25$ $V_{HCl} = \frac{2.25}{0.1} = 22.5$

$[NH_4Cl] = \left[\frac{2.25}{37.5}\right] = 0.06$ M and $pK_b = 5 - \log 1.8 = 4.74$

$\therefore \quad pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C = 7 - \frac{4.74}{2} - \frac{1}{2}\log 0.06 = 5.24$

3. (a) $HPr + OH^- \longrightarrow Pr^- + H_2O$

4   0

[HPr] = 0.1 M

$\therefore \quad [H^+] = \sqrt{K_a \times c} = 10^{-3}$ M

$\therefore \quad pH = 3$

(b) $HPr + OH^- \longrightarrow Pr^- + H_2O$

4   3

1   3

The solution is a Buffer solution.

$\therefore \quad pH = pK_a + \log \frac{[Pr^-]}{[H\,Pr]} = 5 + \log 3 = 5 + 0.48 = 5.48$

(c) $$\begin{array}{llll} HPr & + \; OH^- & \longrightarrow Pr^- + H_2O & \\ 4 & 4 & & \\ - & - & 4 & \end{array}$$

$[Pr^-] = \frac{1}{20}M$

$\therefore pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C = 7 + \frac{1}{2} \times 5 + \frac{1}{2}\log 0.05 = 8.85$

(d) $$\begin{array}{llll} HPr & + \; OH^- & \rightarrow & Pr^- + H_2O \\ 4 & 5 & & \\ - & 1 & & 4 \end{array}$$

$[OH^-] = \frac{1}{90}M \Rightarrow pOH = \log 90 = 1.96$

$\therefore \; pH = 12.04$

4. (a) At equilibrium point.
No. of milieq. of Base = No. of milieq. of HCl

$$\frac{0.252 \times 1000}{\text{Molar mass}} = 0.14 \times 40$$

$\therefore$ Molar mass of base = 45

(b) $$\begin{array}{lllll} & BOH + & HCl \longrightarrow & BCl + & H_2O \\ t = 0 & 5.6 & 0.14 \times 20 & & \\ & 5.6 & 2.8 & 0 & 0 \\ & 2.8 & 0 & 2.8 & \end{array}$$

Basic buffer

$pH = 10.7$ So $pOH = 3.3$
$pOH = pK_b = 3.3$

$K_b = \text{Antilog}(-3.3) = \text{Antilog}(1 - 0.3) \times 10^{-4} = 5 \times 10^{-4}$

5. Using the Henderson's equation $pH = pK_a^{\circ} + \log\{[In^-]/[HIn]\}$, we get
$pH_1 = -\log(1.0 \times 10^{-5}) + \log(1/10) = 5 - 1 = 4$
$pH_2 = -\log(1.0 \times 10^{-5}) + \log(10/1) = 5 + 1 = 6$
The pH of the solution should change from 4 to 6.

Single Correct Answer Type

6. (b) The pH range of the indicator is $pK_{in} \pm 1$. On increase in temperature pK_{in} decreases, therefore pH range of indicator decreases.

7. (c) $pK_{HIn} = 5$
(a) $CH_3COOH + NaOH$, end point $pH > 7$
(b) Aniline hydrochloride + NaOH, end point $pH > 7$
(c) $NaHCO_3 + HCl$, end point $pH > 7$
(d) $Ba(OH)_2 + H_2C_2O_4$, end point $pH > 7$

8. (c) $pK_a = 5.45$

$pH = pK_{HIn} + \log\frac{[\text{Base form}]}{[\text{Acid form}]} \Rightarrow pH = pK_{HIn} = 5.45$

For a Buffer solution,

$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]} \Rightarrow 5.45 = 4.75 + \log\frac{[CH_3COONa]}{[CH_3COOH]}$

$0.7 = \log\frac{[CH_3COONa]}{[CH_3COOH]} \Rightarrow \frac{5}{1} = \frac{[CH_3COONa]}{[CH_3COOH]}$

9. (b)

(i) False, $[OH^-] = \frac{10^{-14}}{[H^+]}$ at 25°C

$= \frac{K_w}{[H^+]}$ at any other temperature

(ii) False, $\Delta G^{\circ} = 0 = -RT \ln K_{eq}$
so, $K_{eq} = 1$
Hence, reaction will proceed significantly in the forward direction.

10. (c)

(i) Initially pH will decrease fast, then slowly due to buffer formation and then will decrease fast as buffer action diminishes.

(ii) For a weak electrolyte,

$$K_a = \frac{C\alpha^2}{(1-\alpha)}$$

When $\alpha << 1$, then $\alpha = \sqrt{\frac{K_a}{C}}$

as C increases $\Rightarrow \alpha$ decreases
as C is tending to zero $\Rightarrow \alpha$ will be unity

(iii) At 1/4th neutralisation
$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
$\left(0.1 \times \frac{3}{4}\right) \qquad \left(0.1 \times \frac{1}{4}\right)$

$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a + \log\left(\frac{1}{3}\right)$

At 3/4th neutralization
$pH = pK_a + \log 3$

So difference in pH $= \Delta(pH) = \log 3 - \log\frac{1}{3} = 2\log 3$

11. (c) meq. of acid = meq. of base $\Rightarrow 20 \times M = 20 \times 0.2 = 4$
Molarity of HA = 0.2 M

$$\begin{array}{lllllll} HA & + & OH & \rightarrow & A^- & + & H_2O \\ 5 & & 2 & & & & \text{m. mole} \\ 3 & & - & & 2 & & \text{m. mole} \end{array}$$

$\therefore \; pH = pK_a + \log\frac{[A^-]}{[HA]} \Rightarrow 5.8 = pK_a + \log\left(\frac{2}{3}\right)$

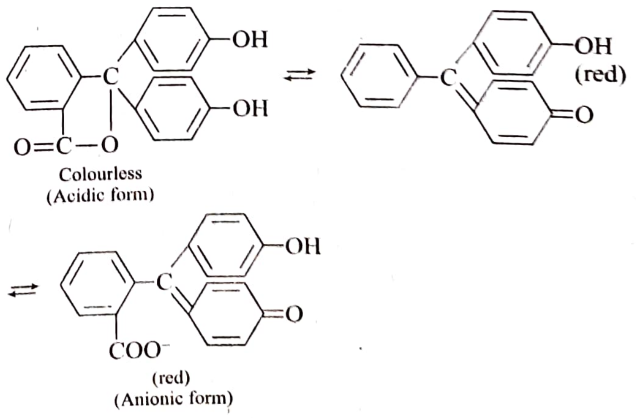
$\Rightarrow pK_a = 5.98$

12. (d) $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Difference in pH between $\frac{1}{3}$ and $\frac{2}{3}$ stages of neutralisation =

$$\left[pK_a + \log\left(\frac{2/3}{1/3}\right)\right] - pK_a + \log\left(\frac{1/3}{1/2}\right) = 2\log 2$$

13. (b)



Multiple Correct Answers Type

14. (a, b)

$$\text{HIn} \rightleftharpoons \text{In}^- + \text{H}^+$$

Red blue

$$\text{pH} = pK_{\text{In}} + \log\frac{[\text{In}^-]}{[\text{HIn}]}$$

(A) $\text{pH} = (5 - \log 3) + \log\left(\frac{25}{75}\right) = 4.05$

(B) $\text{pH} = pK_{\text{In}} + \log\left(\frac{75}{25}\right) = 5 - \log 3 + \log 3 = 5$

15. (a, b, c, d) All are facts.

16. (c, d)

Given graph is plotted for the titration of weak diprotic acid with base.

17. (c, d)

Higher the K_a of acid lower is the pH of acid for same concentration.

18. (c, d)

Titration curve shows that

$K_1 > K_2 > K_3$

Initial pH decides whether the acid is strong or weak.

Matching Column Type

19. (a→s), (b→p), (c→r), (d→q)

- At maximum buffer capacity, [salt] = [acid], hence pH = pK_a.
- At the $\frac{1}{4}$ th equivalence point of titration of weak acid HA,

  $\text{pH} = pK_a - \log\frac{1}{3}$
- At the $\frac{3}{4}$ th equivalence point of titration of weak acid HA,

  $\text{pH} = pK_a + \log\frac{1}{3}$
- For C(M) solution of weak acid HA,

  $$\text{pH} = \frac{1}{2}(pK_a - \log C) = \frac{1}{2}\left(pK_a - \log\frac{1}{3}\right)$$

  $$= \frac{1}{2}(pK_a + \log 3)$$

Integer Type

20. (5) $K_aK_b = 10^{-14}$

or $K_a = K_{in} = 10^{-5}$

$\therefore [\text{H}^+] = 10^{-5}$

or pH = 5

21. (6.1) Let M_1 and M_2 be the molarities of acid HX and the base NaOH, respectively, and let V be the volume of acid. Substituting the given data in Henderson's equation,

$$\text{pH} = pK_a^\circ + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{we get } 5.8 = pK_a^\circ + \log\left[\frac{(10\text{ mL})\,M_2}{VM_1 - (10\text{ mL})M_2}\right] \quad (1)$$

$$6.402 = pK_a^\circ + \log\left[\frac{(20\text{ mL})\,M_2}{VM_1 - (20\text{ mL})M_2}\right] \quad (2)$$

Subtracting Eq. (1) from Eq. (2), we get

$$0.602 = \log\left[\frac{(20\text{ mL})M_2}{VM_1 - (20\text{ mL})M_2}\,\frac{VM_1 - (10\text{ mL})M_2}{(10\text{ mL})M_2}\right]$$

or $\dfrac{2[VM_1 - (10\text{ mL})M_2}{VM_1 - (20\text{ mL})M_2} = 4$

or $\dfrac{VM_1}{M_2} = \dfrac{60\text{ mL}}{2} = 30\text{ mL}$

Substituting this in either Eq. (1) or Eq. (2), we get

$$pK_a^\circ = 58 - \log\left(\frac{10}{30-10}\right) = 5.8 + 0.30 = 6.1$$

Comprehension Type

22. (b) Let molar absorbance of HIn = $\alpha_{\text{H In}}$ and molar absorbance of $\text{In}^- = \alpha_{\text{In}^-}$

$\therefore$ $6 \times 10^{-4} \times \alpha_{\text{H In}} = 1.142$ or $\alpha_{\text{H In}} = \dfrac{0.142}{6\times10^{-4}}$

and $6 \times 10^{-4} \times \alpha_{\text{In}^-} = 0.943$

or $\alpha_{\text{In}^-} = \dfrac{0.943}{6\times10^{-4}}$

At pH = 8, $[\text{In}^-] + [\text{HIn}] = 6 \times 10^{-4}$

and $\dfrac{0.142}{6\times10^{-4}} \times [\text{HIn}] = \dfrac{0.943}{6\times10^{-4}}[\text{In}^-] = 0.527$

or $0.142\,[\text{HIn}] + 0.943\,[\text{In}^-] = 0.527 \times 6 \times 10^{-4}$

and $0.142\,[\text{HIn}] + 0.142[\text{In}^-] = 6 \times 10^{-4} = 0.142$

$\therefore$ $0.801\,[\text{In}^-] = 0.385 \times 6 \times 10^{-4}$

or $[\text{In}^-] = \dfrac{0.385}{0.801} \times 6 \times 10^{-4} = 0.48 \times 6 \times 10^{-4}$

$= 2.88 \times 10^{-4}$ (M)

23. (d) $[\text{HIn}] = (6 - 2.88) \times 10^{-4} = 3.12 \times 10^{-4}$

$$\text{HIn} \xrightleftharpoons{K_{in}} \text{H}^+ + \text{In}^-$$

$$K_{in} = \frac{[\text{H}^+][\text{In}^-]}{[\text{H In}]} = \frac{10^{-8} \times 2.88 \times 10^{-4}}{3.12 \times 10^{-4}}$$

$$= \frac{2.88}{3.12} \times 10^{-8} = 9.25 \times 10^{-9}$$

24. (d) For acid-base titration, the pH at the equivalence point must lie within $pK_{in} \pm 1$ for a suitable indicators.